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Bridged Bisimide Polysilsesquioxane Xerogels: New Hybrid Organic–Inorganic Materials

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Received August 20, 1996. Revised Manuscript Received November 21, 1996[§]

New hybrid organic–inorganic materials which incorporate the bisimide functionality were synthesized by sol–gel condensation of bisimide monomers containing pendant triethoxysilyl groups. Monomers were prepared by transimidation of bis (2-aminopyridyl)imides with (3-aminopropyl)triethoxysilane. This synthesis was applicable to a variety of commercially available bisanhydrides and did not result in the evolution of water which causes premature hydrolysis and condensation of the trialkoxysilyl group. Solid-state NMR (²⁹Si, ¹³C, and ¹⁵N) was utilized to characterize the polysilsesquioxane bis-imides. Nitrogen sorption porosimetry was used to determine the surface area. The thermal and mechanical characteristics of the resultant materials were measured and compared to linear polyimides.

Introduction

The utility of both linear and cross linked polyimides has long been recognized. These materials are important high performance polymers.^{1–3} In particular, the excellent mechanical properties of these materials under ambient conditions and in extreme environments has made polyimides attractive as films, plastics, varnishes, fibers, and casting compositions.⁴ The synthesis of polyimides typically occurs via a two-step sequence: formation of a polyamic acid precursor by addition of an aromatic diamine to an aromatic tetracarboxylic dianhydride, and subsequent dehydrative cyclization (imidization) via a thermal or chemical process.⁵ However, despite many desirable characteristics of the resultant polymer, the high temperatures necessary in thermal imidization, the use of a chemical imidization agent, and the low solubility of both the poly(amic acid) and polyimide has made the fabrication of certain devices problematic. Accordingly, the development of soluble imide-like precursors which can be processed at ambient temperature with retention of the characteristics of the polyimide would be advantageous.

One such room temperature process which has been extensively utilized in the synthesis of inorganic oxides is sol–gel polymerization of inorganic alkoxides or halides.⁶ This chemistry has been extended to incorporate organic fragments into hybrid organic–inorganic materials. Research into the development of hybrid organic–inorganic materials using the sol–gel process has accelerated in the past 10 years and has been

recently reviewed.^{7–14} Whereas early and continuing work involved the incorporation of linear polymers into inorganic matrixes, we^{15–21} and others^{22–24} have concentrated on the incorporation of small organic segments by the synthesis and sol–gel polymerization of α,ω -bistrialkoxysilyl sol–gel processable monomers. The advantage of this process is the homogeneous distribution of the bridging organic moiety into the inorganic matrix. This distribution permits the easy preparation of films without the problems of phase separation which can occur with polymer/silica composites.^{25,26}

A process which combines the ease of the sol–gel process with the desirable mechanical and thermal properties of polyimides is a worthy target of research. Indeed, this objective has been approached by various

[§] Abstract published in *Advance ACS Abstracts*, January 15, 1997.

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research groups with the incorporation into a silica matrix of polyimides terminated with trimethoxysilyl units,²⁷ by the immobilization of metal oxide clusters into polyimide matrixes,²⁸ and by the incorporation of a soluble polyamic-acid into a silica matrix via a soluble silica source.^{29–32} These early efforts revealed that the incorporation of SiO₂ into the polyimide caused a concomitant increase in the decomposition temperature,³¹ density,³¹ and modulus,^{30,31} and a decrease in the tensile strength.^{29–31} Despite these mechanical advantages, dispersions of SiO₂ particles in the polyimide network are heterogeneous and result in opaque films with SiO₂ contents greater than 10% (i.e., silica particles dispersed in the polyimide matrix).^{29–31} Although transparent films could be obtained by using a coupling agent (i.e., (γ -glycidyloxypropyl)triethoxysilane²⁹ or (aminophenyl)trimethoxysilane³⁰) this approach introduces an additional component to the systems and the amount of coupling agent necessary to achieve clarity tends to be empirically determined and system dependent.

We envisioned a one-component hybrid organic-inorganic system that incorporated the polyimide characteristics and could produce bulk materials and transparent films. This one component system would avoid the problem of phase separation and the resultant material properties would result from the molecular structure of the hybrid system rather than interactions between the polyimide- and the SiO₂-rich phases.

Experimental Section

Materials and Methods. ¹H NMR spectra were recorded on a General Electric GN-500 (500 MHz), Omega-500 (500 MHz), or GE NR-300 (300 MHz) spectrometer. Chemical shifts are reported on the δ scale in ppm relative to either tetramethylsilane (0.00 ppm) or CDCl₃ (7.26 ppm) as internal standard. Coupling constants (*J*) are reported in Hz. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; and refer to the appropriate couplings.

¹³C NMR spectra were recorded on a General Electric GN-500 (125 MHz) or Omega-500 (125 MHz) spectrometer. Chemical shifts are reported in ppm relative to either tetramethylsilane (0.00 ppm) or CDCl₃ (77.0 ppm) as an internal standard. ²⁹Si NMR spectra were obtained on the Omega-500 (99 MHz) or General Electric GN-500 (99 MHz) spectrometer with tetramethylsilane (0.00 ppm) as external or internal standard.

¹³C and ²⁹Si solid-state NMR were obtained on a Chemagnetics CMX-200 spectrometer at 50.29 and 39.73 MHz, respectively. Hexamethylbenzene (HMB) was used as an external standard (17.53 ppm relative to TMS) for ¹³C; hexamethylcyclotrisiloxane (HMCTS) used as external standard (−9.33 ppm relative to TMS). Cross-polarization experiments were conducted with an optimum contact time of 3.0–5.0 ms for both nuclei. The number of acquisitions were 2000 for ²⁹Si and ¹³C with a recycle delay of 1 s. Single-pulse experiments were conducted for ¹³C and ²⁹Si in order to verify and quantify peak assignments. Recycle delay times were 30 and 180 s,

respectively. ¹³C interrupted decoupling experiments were utilized to verify carbon assignments with optimum acquisition delay times (τ = 50–150 ms). Sample spinning rates were 2.5–3.0 and 3.0–4.0 kHz for ²⁹Si and ¹³C nuclei, respectively.

Infrared spectra were recorded on a Analect RFX-40 FTIR spectrophotometer. Low-resolution mass spectra were acquired on a Finnigan Model 4000 GC/MS/DS and are reported as mass/charge (*m/z*) ratios using chemical ionization (CI, isobutane or NH₃) or electron ionization (EI, 70 eV) with percent relative abundance. High-resolution mass spectra were obtained with a VG-7070e high-resolution mass spectrometer.

Surface area measurements were conducted on a Micromeritics ASAP 2000 porosimeter using high-purity nitrogen as adsorbate at 77 K. Surface areas were calculated by the BET equation ($Q_{05} \leq P/P_0 \leq 0.35$ for N₂) and pore distributions characterized by Barret–Joyner–Halendg. Thermal analyses were recorded on a DuPont Thermal Analyst 2000 with 910 DSC and 951 TGA modules. A 10 °C/min heating ramp was used with a constant flow of N₂ (80 mL/min). Indium and zinc were used as external calibrants for the DSC while indium and silver were used for the TGA. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

4,4'-Oxydiphthalic di(2-aminopyridyl)imide (2a): In a 1 L round-bottom flask equipped with a stir bar was added 4,4'-oxydiphthalic anhydride (20.0 g, 6.65 × 10^{−2} mol) and xylenes (322 mL). The white suspension was stirred under N₂ at room temperature for 7.5 min and 2-aminopyridine (12.15 g, 1.29 × 10^{−1} mol, 2 equiv) was added. A Dean–Stark apparatus was placed on the flask, and the white suspension was heated to reflux over 15 min at which time a majority of solid dissolves giving a clear, colorless solution which was stirred at reflux for 5 days. The solution was cooled to room temperature, and xylenes were removed in vacuo to give a pale yellow solid. The solid was stirred with ether (500 mL) for 12 h to remove any residual 2-aminopyridine, filtered, and dried in vacuo at 80 °C to give a white powder (29.5 g, 99%); mp 270–280 °C; ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.64 (m, 2H, H_a), 8.08 (m, 2H, H_b), 8.05 (m, 2H, H_b), 7.68 (s, 2H, H_c), 7.66 (m, 2H, H_c), 7.55 (m, 4H, H_d); ¹³C NMR (125 MHz, D₂SO₄) δ 165.9, 165.3, 161.8, 158.3, 149.0, 140.8, 138.9, 131.7, 126.9, 124.2, 123.8, 119.8, 115.8; IR (KBr) 640.3, 701.9, 736.7, 779.1, 829.2, 864.0, 1076.1, 1103.1, 1199.5, 1238.1, 1261.2, 1369.2, 1434.8, 1473.4, 1589.1, 1608.3, 1731.8 (C=O), 1778.1 (C=O) cm^{−1}; MS (CI isobutane) *m/z* calcd for C₂₆H₁₄O₅N₄: 462.0964, found 462.0980, 462, 387, 358, 311, 266, 194.

4,4'-Oxydiphthalic bis(3-(triethoxysilyl)propyl)imide (ODPTDI, 3a): In a 250 mL three-neck round-bottom flask equipped with a stir bar was added 4,4'-oxydiphthalic bis(2-aminopyridyl)imide (5.10 g, 1.10 × 10^{−2} mol) and xylenes (108 mL). The white suspension was stirred under N₂ at room temperature for 5 min and 3-(triethoxysilyl)propylamine (8.0 mL, 3.40 × 10^{−2} mol, 3 equiv) was added. A reflux condenser was placed on the flask and the yellow solution was heated to reflux over 15 min at which time the solid dissolved to give a clear yellow solution. The solution was stirred at reflux for 13 days and cooled to room temperature, xylenes were removed in vacuo, and 3-(triethoxysilyl)propylamine and 2-aminopyridine were removed by bulb-to-bulb distillation (~5 mmHg, 120–130 °C). Chromatography (1:1 ether/petroleum ether, *R_f* = 0.44) on the resultant fluorescent yellow oil gave a pale yellow crystalline solid (2.48 g, 31.4%); mp 72.5–75 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, *J* = 8.3 Hz, 2H, H_a), 7.37 (d, *J* = 2 Hz, 2H, H_b), 7.32 (dd, *J* = 8.3, 2.0 Hz, 2H, H_c), 3.77 (q, *J* = 7.1 Hz, 12H, H_d), 3.63 (t, *J* = 7.3 Hz, 4H, H_e), 1.74 (m, 4H, H_f), 1.16 (t, *J* = 7.16 Hz, 18H, H_g), 0.60 (m, 4H, H_h); ¹³C NMR (125 MHz, CDCl₃) δ 167.3, 167.1, 160.8, 134.9, 127.5, 125.4, 124.0, 113.4, 58.3, 40.6, 22.0, 18.2, 7.7; ²⁹Si NMR (100 MHz, CDCl₃) δ −46.2; UV/vis (ACN, 1.9 × 10^{−5} M) 234, 292–360 nm; IR (KBr) 744.4, 775.2, 790.7, 956.5, 1079.9, 1103.1, 1234.2, 1361.5, 1396.2, 1446.4, 1712.5 (C=O), 1770.3 (C=O), 1770.3, 2892.7, 2931.3, 2973.7 cm^{−1}; MS (LSIMS) *m/z* calcd for C₃₄H₄₈O₁₁N₂Si₂: 671.2456, found 671.2453, 671, 626, 163, 119.

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ODTDI xerogel (0.4 M, THF, HCl) (4a): In a polypropylene vial (5 mL) rinsed with THF was added 4,4'-oxydiphthalic bis(3-(triethoxysilyl)propyl)imide (0.7553 g, 1.1054×10^{-3} mol) and THF (2.528 mL). The vial was agitated until a homogeneous solution resulted and HCl(aq) (1 M, 0.108 mL, 6.0 equiv of H_2O) was added. The vial was sealed, shaken for 2 min to give a homogeneous solution, and allowed to stand. After 3 min, the solution gelled, and after 30 min, significant syneresis (~45%) was evident. The gel was aged for 2 days, soaked in THF for 24 h, air-dried (24 h), rough ground, and dried in vacuo at 100 °C for 48 h to give a hard transparent solid (0.60 g, 118%): ^{13}C NMR (50.29 MHz, solid state) CP-MAS (4000 Hz) δ 165.5, 160.6, 157.2, 132.8, 124.3, 114.2, 65.9, 38.6, 23.9, 20.7, 8.3; MAS (4000 Hz) 165.5, 160.6, 133.6, 125.0, 115.0, 65.9, 38.6, 23.9, 20.7, 8.3; INTDEC (4000 Hz, $\tau = 200$ μ s) 165.3, 157.7, 133.0, 125.8, 65.7, 24.2; ^{29}Si NMR (39.97 MHz, solid state); CP-MAS (4000 Hz) δ -48.4 (T^1), -57.2 (T^2), -66.1 (T^3), MAS (4000 Hz) -51.3 (T^1), -57.2 (T^2), -67.2 (T^3); ^{15}N NMR (20.27 MHz, solid state) CP-MAS (4000 Hz) -218.7 ppm; IR (KBr) 694.3, 744.4, 1002.8, 1064.5, 1176.4, 1234.2, 1276.7, 1365.4, 1396.2, 1446.4, 1477.2, 1612.2, 1712.5 (C=O imide), 1774.2 (C=O imide), 2877.3, 2939.0, 3471.2 (SiOH) cm^{-1} ; deconvolution for ^{29}Si MAS NMR: T^1 3.9%; T^2 63.4%; T^3 32.7%; 76.3% condensed. Anal. calcd for $C_{22}H_{18}O_8N_2Si_2$: C, 53.43; H, 3.67; Si, 11.36; N, 5.66; found: Carbon, 52.30; Hydrogen, 4.72; Silicon, 11.01; Nitrogen 5.16. TGA: onset 148.0 °C, end 291.0 °C, loss of 10.3%; onset 509 °C, end 554 °C, loss of 31.8%. DSC 509, 531 °C (exotherm); porsimetry: nitrogen: 77 K. BET: $0.05 \leq P/P_0 \leq 0.35$; $1.16 \pm 0.06 m^2/g$; $R = 0.991$; $C = 17.5$. Vickers hardness determination average of 30 measurements, load of 100 g, HV = 9.4 (93 MPa).

3,3',4,4'-Biphenyltetracarboxylic bis(2-aminopyridyl)imide (2b): Prepared as described for **2a** (10.85 g, 94%): mp 349–356 °C; 1H NMR (500 MHz, DMSO- d_6) δ 8.66 (dd, $J = 4.8$, 2 Hz, 2H, H_a), 8.48 (d, $J = 1.6$ Hz, 2H, H_b), 8.42 (dd, $J = 1.6$, 7.6 Hz, 2H, H_c), 8.13 (d, $J = 7.6$ Hz, 2H, H_d), 8.06 (m, 2H, H_e), 7.59 (d, $J = 7.6$ Hz, 2H, H_f), 7.55 (m, 2H, H_g); ^{13}C NMR (125 MHz, D_2SO_4) δ 165.3, 164.9, 148.1, 145.4, 139.9, 138.1, 134.9, 128.9, 127.8, 125.3, 123.3, 123.1, 118.3; IR (KBr) 640.3, 732.8, 752.1, 782.9, 848.5, 863.9, 887.1, 995.1, 1072.2, 1099.2, 1137.8, 1230.4, 1257.4, 1361.5, 1419.4, 1434.8, 1477.2, 1589.0, 1616.1, 1724.1 (C=O), 1774.2 (C=O) cm^{-1} ; MS (EI) m/z calcd for $C_{25}H_{14}O_4N_4$: 446.1015, found 446.1022, 446.418, 370, 342.

3,3',4,4'-Biphenyltetracarboxylic bis(3-(triethoxysilyl)propylamino)imide (BPTDI, 3b): Prepared as described for **3a** (2.23 g, 29%): mp 84.5–85.5 °C; 1H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 2H, H_a), 7.96 (s, 4H, H_b), 3.81 (q, $J = 7.0$ Hz, 12H, H_c), 3.71 (t, $J = 7.3$ Hz, 4H, H_d), 1.81 (m, 4H, H_e), 1.21 (t, $J = 7.0$ Hz, 18H, H_f), 0.67 (m, 4H, H_g); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.7 (2 carbons), 144.9, 133.2, 132.7, 131.8, 123.9, 121.9, 58.3, 40.7, 22.0, 18.2, 7.7; ^{29}Si NMR (100 MHz, $CDCl_3$) δ -46.2; IR (KBr) 740.5, 779.1, 956.5, 975.8, 998.9, 1079.9, 1353.8, 1388.5, 1442.5, 1704.8, 1766.5, 2892.7, 2927.4, 2973.7 cm^{-1} ; MS (FAB) m/z calcd for $C_{37}H_{48}F_6O_{10}N_2Si_2$: 723.2745, found 723.2724; 655, 610.

BPTDI xerogel (0.4 M, THF, HCl) (4b): Prepared as described for **4a** (0.62 g, 123%): ^{13}C NMR (50.29 MHz, solid state) CP-MAS (4000 Hz) δ 165.5, 142.9, 130.5, 121.1, 50.0, 38.6, 19.2, 8.3; MAS (4000 Hz) 166.3, 142.9, 131.3, 127.7, 50.8, 39.4, 19.2, 8.0; INTDEC (4000 Hz, $t = 200$ ms) 165.5, 141.9, 130.5, 50.8, 18.9; ^{29}Si NMR (39.97 MHz, solid state); CP-MAS (4000 Hz) δ -49.6 (T^1), -57.3 (T^2), -66.3 (T^3), MAS (4000 Hz), -58.1 (T^2), -65.1 (T^3); ^{15}N NMR (20.27 MHz, solid state) CP-MAS (4000 Hz) -216.9 ppm; IR (KBr) 678.8, 740.5, 844.7, 902.5, 1083.8, 1187.9, 1218.8, 1315.2, 1365.4, 1392.4, 1442.5, 1622.3, 1715.5 (C=O imide), 1770.3 (C=O imide), 2888.8, 2939.0, 3467.4 (SiOH) cm^{-1} ; deconvolution for ^{29}Si MAS NMR: T^2 78.1%; T^3 21.9%; 74.0% condensed. Anal. calcd for $C_{22}H_{18}N_2O_7Si_2$: C, 55.22; H, 3.79; Si, 11.74; N, 5.85. Found: C, 54.54; H, 4.66; Si, 11.44; N, 5.01; F, 12.07. TGA: onset 517 °C, end 537 °C, loss of 30.5%. DSC 508, 530 °C (exotherm); porsimetry: nitrogen: 77 K. BET: $0.05 \leq P/P_0 \leq 0.35$; $1.98 \pm 0.06 m^2/g$; $R = 0.997$; $C = 17.22$. Vickers hardness determination average of 30 measurements, load of 100 g, HV = 11.6 (113 MPa).

Thin-film formation with 3b: In a polypropylene vial (1 mL) rinsed with THF was added 3,3',4,4'-biphenyltetracarboxylic bis(3-(triethoxysilyl)propylamino)imide (0.095 g, 1.38×10^{-4} mol) and THF (0.682 mL). The vial was agitated until a homogeneous solution resulted and HCl(aq) (1 M, 0.010 mL, 4.0 equiv H_2O) was added. The vial was shaken for 30 s, and transparent films were cast after aging for 6 min (volume 50 μ L, 2000 rpm, 1 min). Films were able to be cast until gelation (~22 min).

4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (1c): In a 25 mL round-bottom flask equipped with a stir bar was added 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (4.85 g, 1.09×10^{-2} mol) which was contaminated with a small percentage of di- and tetraacid impurity and acetic anhydride (5.41 g, 5.29×10^{-2} mol, 4.9 equiv). The white suspension was heated to reflux and after ~20 min became homogeneous. The yellow solution was heated at reflux for 4 h and allowed to cool overnight, at which time a yellow precipitate formed. The yellow solid was isolated via filtration, washed with acetic acid (15 mL), and dried in vacuo to give a pale yellow powder (3.80 g, 78.5%): mp 245.9–249 °C; 1H NMR (500 MHz, DMSO- d_6) δ 7.80 (d, $J = 8.43$ Hz, 1H, H_a), 7.68 (s, 1H, H_c), 7.61 (d, 8.43 Hz, H_b); ^{13}C NMR (70 MHz, DMSO- d_6) δ 168.1, 167.2, 162.8, 135.2, 133.5, 132.2, 129.5, 129.1; IR (KBr) 590.1, 690.4, 717.4, 736.7, 836.9, 848.5, 902.5, 929.5, 964.2, 987.4, 1114.6, 1153.2, 1198.8, 1211.1, 1261.2, 1299.8, 1342.2, 1781.9 (C=O), 1855.2 (C=O) cm^{-1} ; MS (EI) m/z calcd for $C_{19}H_6O_6F_6$: 444.0068, found 444.0073, 444, 400 ($-CO_2$).

4,4'-(Hexafluoroisopropylidene)diphthalic bis(2-aminopyridyl)imide (2c): In a 500 mL round-bottom flask equipped with a stir bar was added 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (14.3 g, 3.2×10^{-2} mol) and toluene (160 mL). The white suspension was stirred under N_2 at room temperature for 8 min, and 2-aminopyridine (6.06 g, 6.4×10^{-2} mol, 2 eq) was added. A Dean–Stark apparatus was placed on the flask, and the white suspension was heated to reflux over 15 min at which time the solid dissolves to give a clear, colorless solution. Upon full reflux, a white suspension had developed. Reflux was continued for 2 days, the suspension was filtered, and toluene was removed in vacuo to give an amorphous yellow solid (15.1 g, 2.45×10^{-2} mol, 77%). 1H NMR indicated residual amide acid impurities. The yellow solid (15.1 g, 2.45×10^{-2} mol) was taken up in xylenes (200 mL), a Dean–Stark apparatus was attached to the flask, and the white suspension was heated to reflux for 3 days. Filtration gave a brilliant white powder (12.0 g, 62.7% over 2 steps): mp 242–245 °C; 1H NMR (500 MHz, DMSO- d_6) δ 8.67 (m, 2H, H_a), 8.21 (d, $J = 8.06$ Hz, 2H, H_b), 8.07 (m, 2H, H_c), 8.00 (d, $J = 8.06$ Hz, 2H, H_d), 7.85 (s, 2H, H_e), 7.59 (d, $J = 8.06$ Hz, 2H, H_f), 7.55 (m, H_g); ^{13}C NMR (70 MHz, DMSO- d_6) δ 165.6, 165.5, 149.5, 145.7, 138.8, 136.2, 132.8, 132.4, 124.3, 124.0, 123.3 (q, 287.5), 122.9, 64.6 (h, 25.2); IR (KBr) 647.9, 690.4, 713.5, 740.5, 782.9, 852.3, 964.2, 991.2, 1118.5, 1137.8, 1164.8, 1195.6, 1211.1, 1257.4, 1299.8, 1380.8, 1434.8, 1473.4, 1589.1, 1727.9 (C=O), 1789.6 (C=O) cm^{-1} ; MS (EI) m/z calcd for $C_{29}H_{14}F_6O_4N_4$: 596.0919, found 596.0922, 568, 231, 113.

4,4'-(Hexafluoroisopropylidene)diphthalic bis(3-(triethoxysilyl)propyl)imide (3c): Prepared as described for **3a** (2.32 g, 32.4%): 1H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, $J = 7.95$ Hz, 2H, H_a), 7.76 (s, 2H, H_c), 7.73 (d, $J = 7.95$ Hz, 2H, H_b), 3.76 (q, $J = 7.16$ Hz, 12H, H_d), 3.66 (t, $J = 7.4$ Hz, 4H, H_e), 1.76 (m, 4H, H_f), 1.16 (t, $J = 7.16$ Hz, 18H, H_g), 0.62 (m, 4H, H_h); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 166.9, 138.5, 135.3, 132.9, 124.6, 123.3, 65.0 (sept, $J = 25.7$ Hz), 58.4, 40.8, 22.0, 18.1, 7.7; ^{29}Si NMR (100 MHz, $CDCl_3$) δ -46.3; IR (NaCl, neat) 586.3, 721.3, 466.4, 790.7, 964.2, 1079.9, 1103.1, 1168.7, 1191.8, 1211.1, 1257.4, 1295.9, 1365.3, 1392.4, 1442.5, 1720.2, 1778.1, 2888.8, 2931.3, 2977.6 cm^{-1} ; MS (FAB) m/z calcd for $C_{37}H_{48}F_6O_{10}N_2Si_2$: 850.2751, found 850.2746, 850, 804, 760, 614, 163, 119.

HFIPDTDI xerogel (0.4 M, THF, HCl) (4c): Prepared as described for **4a** (0.45 g, 89%): ^{13}C NMR (50.29 MHz, solid state) CP-MAS (4000 Hz) δ 167.1, 133.6, 127.4, 125.0, 58.8, 41.0, 20.7, 9.9; MAS (4000 Hz) 168.0, 139.4, 133.8, 128.6, 124.3, 41.2, 22.0, 10.6; INTDEC (4000 Hz, $t = 200$ ms) 167.3, 133.5,

Scheme 1. Synthesis of Sol–Gel Processable Bisimides via Modified Transimidation Procedure

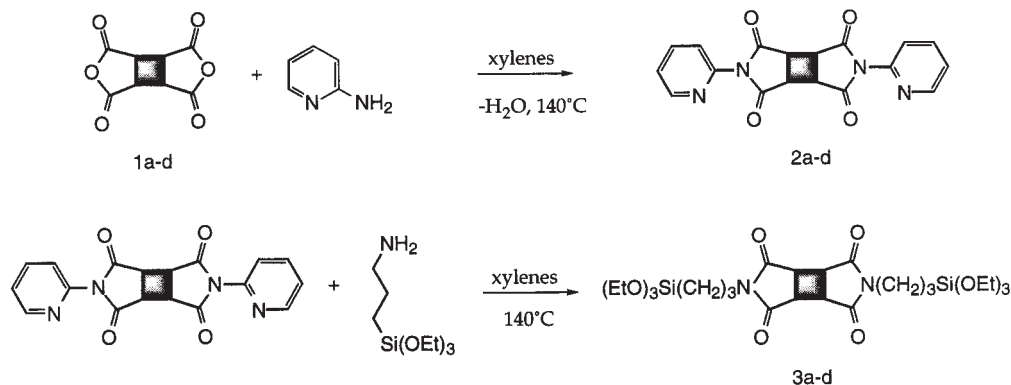


Table 1. Starting Tetracarboxylic Bisanhydrides and Yields of Reactions

Starting Tetracarboxylic dianhydride	Acronym	Yield Bis(2-aminopyridyl)imide	Yield Bis[(3-triethoxysilyl)propyl]imide
	ODPTI	2a, 99%	3a, 31%
	BPTDI	2b, 94%	3b, 29%
	HFIPTDI	2c, 63%*	3c, 32%
	BPATDI	2d, 97%	3d, 30%

* Required a two step imidization procedure.

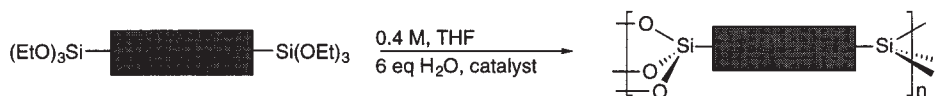
20.5; ^{29}Si NMR (39.97 MHz, solid state); CP-MAS (4000 Hz) δ -56.5 (T³), -65.9 (T³), MAS (4000 Hz), -48.5 (T¹), -56.8 (T³), -65.6 (T³); ^{15}N NMR (20.27 MHz, solid state) CP-MAS (4000 Hz) -212.8 ppm; IR (KBr) 586.3, 721.3, 744.4, 848.5, 910.2, 972.0, 1064.5, 1191.8 (CF₃), 1249.7 (CF₃), 1295.9 (CF₃), 1365.4, 1396.2, 1396.2, 1446.4, 1627.6, 1716.3 (C=O imide), 1778.1 (C=O imide), 2888.9, 2942.8, 3478.0 (SiOH) cm⁻¹; deconvolution for ^{29}Si MAS NMR: T¹ 0.7%; T² 73.1%; T³ 26.2%; 75.1% condensed. Anal. calcd for C₂H₂O₃Si₂: C, 47.77; H, 2.89; Si, 8.94; N 4.46 F, 18.13 Found: C, 50.21; H, 3.68; Si, 9.11; N, 4.14; F, 12.07. TGA: onset 198.0°C, end 338.0°C, loss of 9.3%; onset 528, end 537, loss of 56.7%. DSC 519, 538°C (exotherm); porsimetry: nitrogen: 77 K. BET: 0.05 ≤ P/P₀ ≤ 0.35: 1.3 ± 0.7 m²/g; R = 0.979; C = 7.02. Vickers hardness determination average of 30 measurements, load of 100 g, HV = 16.0 (157 MPa).

Bisphenol A dianhydride (BPADAN, 1d): Used as received from General Electric: mp 190.6–194°C (by DSC); ^1H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.43 Hz, 2H), 7.45 (dd, *J* = 2.2, 8.43 Hz, 2H), 7.38 (d, *J* = 2.2 Hz, 2H), 7.35 (d, *J* = 8.8 Hz, 4H), 7.04 (d, *J* = 8.8 Hz, 4H), 1.76 (s, 6H); ^{13}C NMR (100 MHz, CDCl₃) δ 165.2, 162.7, 162.1, 151.9, 148.2, 133.9,

128.9, 127.6, 124.1, 120.3, 112.2, 42.6, 30.9; IR (KBr) 590.1, 632.5, 675.0, 740.5, 783.0, 844.7, 875.5, 891.0, 941.1, 1018.2, 1068.4, 1103.1, 1157.1, 1172.5, 1222.7, 1284.4, 1353.8, 1407.8, 1450.2, 1481.1, 1504.2, 1592.9, 1616.1, 1781.9 (C=O), 1847.5 (C=O), 2931.3, 2962.1 cm⁻¹; MS *m/z* calcd for C₃₁H₂₀O₈ + H⁺: 521.1237, found 521.1213.

Bisphenol A (N,N-bis-2-aminopyridyl)bisimide (2d): In a 250 mL round-bottom flask equipped with a magnetic stir bar was added in order BPADAN (25.02 g, 0.04811 mol), 2-aminopyridine (9.11 g, 0.0968 mol, 2.00 equiv) and toluene (130 mL). The flask was equipped with a Dean–Stark apparatus and stirred. A biphasic suspension developed which disappeared upon heating to yield a homogeneous slightly yellow solution which was refluxed for 16 h (a white precipitate formed). An additional amount of toluene (90 mL) was added and suspension was heated at reflux for an additional 4 h at which time 1.5 mL of water was evident in Dean–Stark apparatus (calculated 1.7 mL). Upon cooling overnight, the white precipitate was filtered, washed with toluene (2 × 50 mL), and dried in vacuum oven to give a white powder (31.36 g, 97.0%): mp 226.2°C (DSC); ^1H NMR (500 MHz, CDCl₃) δ 8.67 (m, 2H), 7.9 (d, *J* = 8.07 Hz, 2H), 7.87 (m, 2H), 7.44 (d,

Scheme 2 Conditions used for the Sol-Gel Hydrolysis and Condensation of Monomers 3a-d



$J = 2.2$ Hz, 2H), 7.41 (d, $J = 8.14$ Hz, 2H), 7.36 (d, $J = 8.14$ Hz, 2H), 7.35 (m, 2H), 7.33 (d, $J = 8.68$ Hz, 4H), 7.04 (d, $J = 8.68$ Hz, 4H), 1.75 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.2, 166.1, 163.9, 152.6, 149.6, 147.5, 146.1, 138.2, 134.2, 128.7, 125.9, 125.0, 123.4, 123.2, 122.0, 123.0, 111.9, 42.5, 30.9; IR (KBr) 620, 640.3, 671.1, 740.5, 771.4, 790.7, 848.5, 883.2, 952.7, 995.1, 1014.4, 1076.1, 1103.1, 1122.4, 1164.8, 1176.4, 1226.5, 1238.1, 1276.7, 1361.5, 1076.4, 1103.1, 1122.4, 1164.8, 1176.4, 1126.5, 1238.1, 1276.7, 1361.5, 1434.8, 1473.4, 1504.2, 1589.1, 1619.9, 1720.2 (C=O), 1778.1 (C=O), 2973.7 cm^{-1} ; MS m/z calcd for $\text{C}_{41}\text{H}_{28}\text{N}_4\text{O}_6 + \text{H}^+$: 673.2087, found 673.2086; DSC: onset 213.8 °C, min 226.18 (endotherm); min 303.9 °C (endotherm); max 508.4 °C (exotherm); TGA: onset 475.5 °C loss of 60.1%.

Bisphenol A (*N,N*-bis-3-triethoxysilylpropyl)bisimide (BPADCDI, 3d): In an oven-dried 500 mL flask equipped with a magnetic stir bar was added the BPADAN 2-aminopyridine derivative (20.00 g, 2.98×10^{-2} mol) and toluene (300 mL). To the stirred white suspension was added (aminopropyl)-triethoxysilane (21.0 mL, 8.85×10^{-2} mol, 2.97 eq). The suspension was stirred and heated. Upon reaching 90 °C, the solution became homogeneous and was further heated to reflux under N_2 for 12 h. The progress of the reaction was monitored by GC analysis. Toluene was removed in vacuo to yield a viscous yellow oil which upon column chromatography gave lustrous white microcrystallites (8.28 g, 30.0%): mp 118 °C (DSC); R_f 0.475 (1:1 ether:petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.76 (d, $J = 8.07$ Hz, 2H), 7.32–7.27 (m, 8H), 7.00 (d, $J = 8.43$ Hz, 4H), 3.80 (q, $J = 6.97$ Hz, 12H), 3.64 (t, $J = 7.33$ Hz, 4H), 1.76 (m, 4H), 1.74 (s, 6H), 1.2 (t, $J = 6.97$ Hz, 18H), 0.64 (dt, $J = 8.8$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.8, 163.3, 152.8, 147.4, 134.6, 128.6, 125.5, 125.0, 122.4, 119.9, 111.5, 58.4, 42.5, 40.6, 31.0, 22.1, 18.2, 7.8; ^{29}Si NMR (CDCl_3) δ -46.0; IR (KBr) 748.3, 783.0, 840.8, 883.2, 956.5, 972.0, 1014.4, 1079.9, 1103.08, 1168.7, 1211.1, 1241.9, 1276.7, 1361.5, 1392.4, 1

Bisphenol A (*N,N*-bis-3(triethoxysilyl)propyl)bisimide xerogel (0.4 M, THF, HCl catalyst, 4d): Prepared as described for **1d** (0.624 g, 110%): ^{13}C NMR (solid state) CP-MAS δ 168.3, 153.0, 147.5, 126.9, 58.8, 55.5, 43.0, 31.8, 22.7, 11.0, MAS 197.0, 169.0, 153.4, 148.7, 135.8, 128.5, 116.8, 58.4, 42.1, 21.9, 9.4; ^{29}Si NMR (solid state) CP-MAS δ -48.2 (T^1), -56.9 (T^2), -65.9 (T^3); MAS -57.1 (T^2), -65.7 (T^3); deconvolution for ^{29}Si MAS NMR: T^2 85.8%; T^3 14.2%; 70.5% condensed; ^{15}N NMR (20.27 MHz, solid state) δ -215.7. Anal. Calcd for $\text{C}_{37}\text{H}_{32}\text{O}_9\text{N}_2\text{Si}_2$: C, 63.05; H, 4.57; Si, 7.97; N, 3.97. Found: C, 63.84; H, 5.06; Si, 7.97; N, 3.52. IR (KBr) 671.1, 744.4, 1014.4, 1076.1, 1172.5, 1234.2, 1272.8, 1392.4, 1619.9, 1639.2, 1712.5 (C=O), 1776.6 (C=O), 3413.4, 1478.9, 3552.2, 3640.9 cm^{-1} ; TGA: onset 165.2 °C, end 277.7 °C, loss of 9.9%; onset 519.5 °C, end 560.6 °C, loss of 45.6%; DSC: 487.6 °C (endotherm); 543.5 °C (exotherm). Porsimetry: nitrogen: 77 K. BET: $0.05 \leq P/P_0 \leq 0.35$; $1.05 \pm 0.05 \text{ m}^2/\text{g}$; $R = 0.992$, $C = 11.56$. Vickers hardness determination average of 30 measurements, load of 100 g, HV = 11.2.

Bisphenol A (*N,N*-bis-3(triethoxysilyl)propyl)bisimide (0.4 M, THF, $\text{NH}_3\text{H}_2\text{O}$ catalyst.) In a polypropylene vial with screw top ($V \sim 8.5$ mL) was added bisimide monomer **3d** (0.744 g, 8.03×10^{-4} mol) and THF (1.00 mL). The vial was agitated for 30 s at which time the white crystalline monomer completely dissolved. Concentrated $\text{NH}_3(\text{aq})$ (~ 14.8 M, 0.192 mL, 12 equiv of H_2O) and the remainder of THF (0.818 mL) were added to give a total volume of 2.00 mL. The solution was shaken for 3 min, although a completely homogeneous solution never formed. Upon sitting for 20 min, thin wispy crystalline needle appeared in the bottom of the vial in a fractal pattern. Upon shaking the precipitate dissolved although the solution was still not homogeneous as indicated by light scattering. After 35 min, the precipitate was again evident

and the gel was shaken for an additional 7 min. After an additional 35 min, the precipitate was again evident but was persistent even after 10 min of vigorous shaking. After 4 days, the solution had developed into a transparent gel with evidence of syneresis. The transparent gel was processed via solvent series, rough ground in mortar and pestle, and dried under dynamic vacuum at 100 °C ($P \sim 0.01$ mmHg) to give a white powder (0.393 g, 69.4%): ^{13}C NMR (solid state) CP-MAS δ 168.2, 152.8, 146.2, 124.6, 59.3, 42.1, 32.0, 23.5, 19.6, 11.0; MAS 197.0, 168.2, 153.6, 148.3, 135.4, 126.5, 59.2, 42.6, 30.9, 22.9, 18.4, 9.6; ^{29}Si NMR (solid state) CP-MAS δ -46.0 (T^1), -58.9 (T^2), -66.6 (T^3); MAS -46.6 (T^1), -52.9 (T^1), -59.8 (T^2), -67.3 (T^3). Deconvolution for ^{29}Si MAS NMR: T^1 34.5, T^1 1%, T^2 4.5%; T^3 59.9% condensation; ^{15}N NMR (20.27 MHz, solid state) δ -215.7; IR (KBr) 690.4, 744.4, 836.9, 921.8, 1010.5, 1076.1, 1172.5, 1234.2, 1272.8, 1365.4, 1392.4, 1446.4, 1447.2, 1504.2, 1600.6, 1619.9, 1716.3 (C=O), 1774.2 (C=O), 3467.4 cm^{-1} ; TGA: onset 504.6 °C, end 554.2 °C, loss of 49.9%; DSC: onset 487.6 °C; 523.6 °C (endotherm).

Results and Discussion

Synthesis of Sol-Gel Processable Monomers.

The synthesis of sol-gel processable bisimide monomers is best accomplished by introducing the triethoxysilyl group at the end of the synthesis. Polyimides are usually synthesized by a two-step procedure that is accompanied by a concomitant release of water. Although such direct syntheses of [(trialkoxysilyl)propyl]-imides have been reported,^{33–36} they often result in the premature hydrolysis and condensation of monomers.³⁷ To achieve the synthesis of pure bis-imide monomers, we utilized the approach of Wengrovius *et al.*,³⁷ who reported a two-step synthesis of [(trialkoxysilyl)propyl]-imides that avoided the release of water. This synthesis is based on a transimidation of a bis (2-aminopyridyl) imide with the an aromatic diamine to give a polyimide.³⁸ We adapted the reported procedure to furnish the required bridged bis-imide sol-gel processable monomers (Scheme 1).

The use of xylenes resulted in a higher reaction temperature and increased yield of the bis(2-aminopyridyl)imide (**2a–d**). In addition we found that the purity of starting anhydride **1a–d** was vital in the overall yield of the precursor imides and in some cases chemical dehydration was performed to eliminate di- and tetraacid impurity.³⁹ The identity of the bridging spacer and the isolated yields are given in Table 1.

Whereas the 2-aminopyridyl imides **2a–d** were synthesized in good to excellent yield, the sol-gel processable monomers **3a–d** were obtained in moderate yields due not to the transimidation reaction ($\sim 90\%$ comple-

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(39) Grummitt, O.; Egan, R.; Buck, A. *Org. Synth. Coll. Vol.* **1955**, *3*, 449.

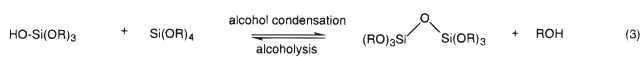
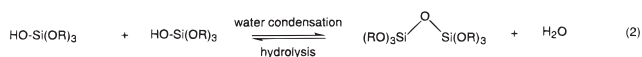
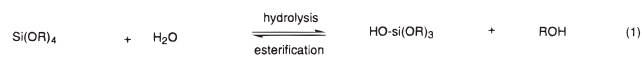
Table 2 Gel Times and Yields for Polysilsesquioxane Formation

monomer	xerogel	catalyst	gel time	yield ^a
3a	4a	1 N HCl	3 min	118%
		conc NH ₃ (aq)	~4 days	
3b	4b	1 N HCl	4 min	123%
		conc NH ₃ (aq)	14 days	
3c	4c	1 N HCl	5 min	89%
		conc NH ₃ (aq)	4 days	
3d	4d	1 N HCl	3 min	110%
		conc NH ₃ (aq)	4 days	70% ^b

^a Calculated assuming 100% condensation of silsesquioxane.^b 12 equiv of H₂O used.

tion via ¹H NMR and GC analysis) but rather from difficulty encountered in the purification of the monomers.

Material Synthesis and Processing. The polymerization of bridged bis(triethoxysilyl)imide was carried out at ambient temperature. Sol-gel chemistry can be divided into two reactions, hydrolysis and condensation (eq 1–3).⁴⁰

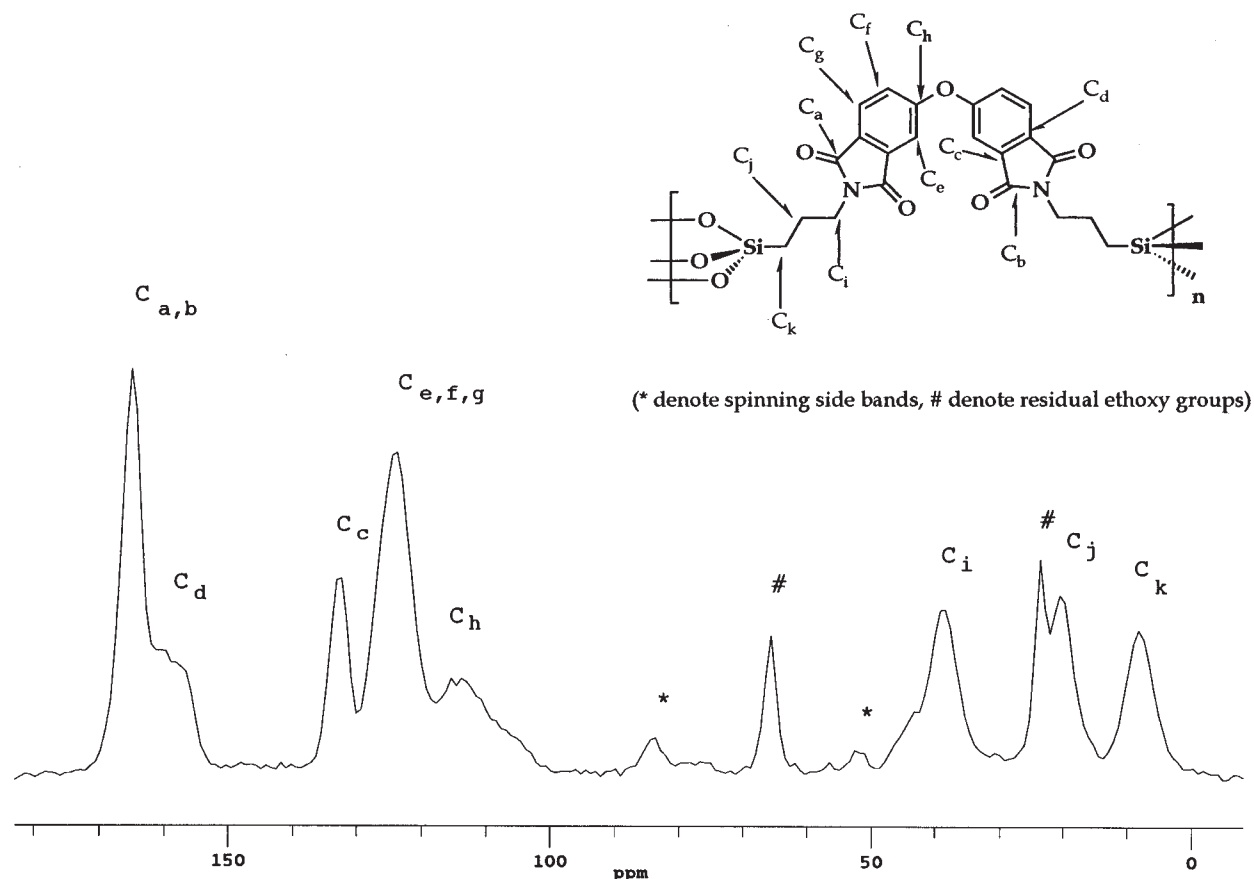


The conditions established for the sol-gel polymerization of the bridged bis(triethoxysilyl)imide **3a–d** consisted of dissolving the monomer in an organic solvent (ethanol or THF), containing 6 equiv of water,⁴¹ in the presence of acid or base catalyst (Scheme 2).⁷

In contrast to earlier studies involving alkyl¹⁷ and aryl^{15,16} bridged polysilsesquioxanes, the gelation of the bisimide monomers **3a–d** was faster with an acidic rather than basic catalyst (Table 2).

Under basic conditions (NH₄OH, THF), polymerization of monomers **3a–c** produced heterogeneous mixtures. These conditions resulted in long gelation times and the formation of opaque gels that lacked mechanical integrity. Because of the heterogeneous nature of the base-catalyzed systems, only xerogels formed under acidic conditions were considered further. Sol-gel polymerization under acidic conditions (1 N HCl, THF) resulted in gelation in 2–5 min. The resulting gels showed significant shrinkage (~40%) after 1–4 h following gelation. The resultant transparent wet gels were processed either via a gradual replacement of THF with solvents of decreasing dielectric constant¹⁶ or were washed with THF and slowly air-dried. In contrast to alkylene and arylene polysilsesquioxanes,^{15–17} the bisimide xerogels were not as brittle and were resistant to rough grinding. The xerogels were transparent (**4a,c,d**) or translucent (**4b**) and could be fabricated into thick (~1 mm) films by varying the dimensions of the gelation vessel. These transparent thick films could be broken, but broke with clean edges. By decreasing⁴² the concentration (0.2 M) and the equivalents of water (4 equiv), transparent thin (~1 μm) films from monomers **3a–c** could be cast on glass substrates.

Characterization of Polysilsesquioxanes. Xerogels were characterized by solid-state NMR (SSNMR). The integrity of the bridging organic group to the sol-gel conditions and subsequent processing was indicated by a combination of ²⁹Si and ¹³C SSNMR. An example

**Figure 1.** ¹³C CP-MAS SSNMR spectrum of bridged bisimide polysilsesquioxane **4a** with carbon assignments.

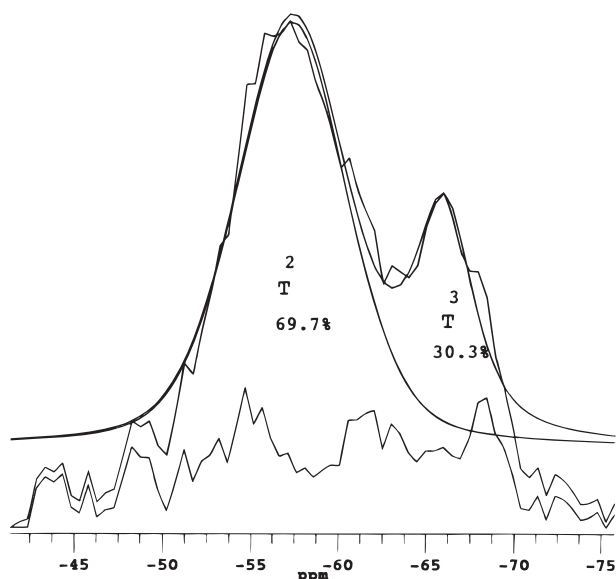


Figure 2 Single-pulse ^{29}Si solid-state MAS NMR and peak deconvolution for **4c** with a 75.1% calculated degree of condensation.

Table 3 Distribution of Siloxane Linkages and Degree of Condensation for Hybrid Polysilsesquioxanes

xerogel	T^0 (%)	T^1 (%)	T^2 (%)	T^3 (%)	degree of condensation (%)
x-OPDTI	0	3.9	63.4	32.7	76.3
x-BPTDI	0	0	78.1	21.9	74.0
x-HFIPTDI	0	0.7	73.1	26.2	75.1
x-BPATDI	0	0	85.8	14.2	70.5
x-BPATDI (base)	34.5	1.1	4.5	59.9	63.3

is the cross-polarization magic-angle spinning solid-state NMR (CP-MAS SSNMR) spectrum of x-OPDTI **4a** (Figure 1). The assignments of the carbon peaks were deduced from the solution ^{13}C NMR spectrum of the monomer along with analysis of single-pulse and interrupted decoupling solid-state ^{13}C NMR techniques. A single peak in the ^{15}N CP-MAS SSNMR was observed at -212 – 219 ppm, indicating the presence of one imide nitrogen.⁴³ Finally, a deconvolution of the ^{29}Si single-pulse SSNMR of the polysilsesquioxane gave the distribution of siloxane linkages and degree of condensation of the materials. These data are summarized in Table 3.

The xerogels from acid catalyzed sol–gel polymerization exhibited ^{29}Si NMR spectra that were dominated by T_2 and T_3 absorptions.⁴⁴ A typical ^{29}Si single-pulse solid-state NMR spectrum shows the distribution of siloxane groups for x-HFIPTDI (Figure 2). The long-pulse delay (180 s) in the single-pulse ^{29}Si SSNMR permits quantitative analysis of the siloxane linkages in the polysilsesquioxanes and calculation of the degree

Table 4 Thermal Stability of Hybrid Bisimide Polysilsesquioxanes **4a–d**

xerogel	DSC onset (°C)	TGA onset (°C)	%SiO ₂ ^b	weight loss ^a at 400 °C
x-OPDTI 4a	509	510	16.1	−1.4%
x-BPTDI 4b	508	517	16.1	−0.21%
x-HFIPTDI 4c	492	528	12.4	−0.60%
x-BPATDI 4d	487	520	10.4	−0.80%

^a Temperature increased to 400 °C at 20 °C/min, held at 400 °C for 240 min under N_2 . ^b Calculated utilizing measured condensation of polysilsesquioxane by ^{29}Si SSNMR.

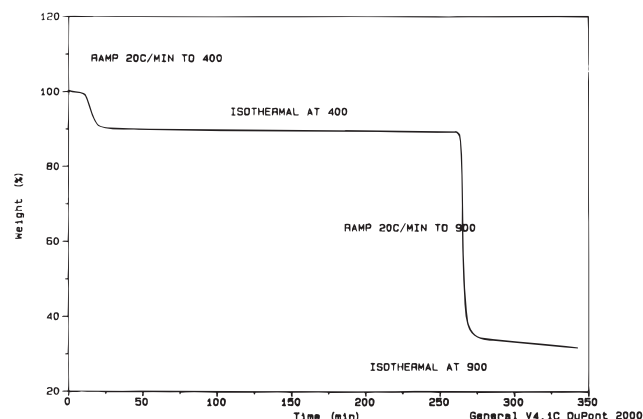


Figure 3 Isothermal TGA trace for bisimide polysilsesquioxane **4c**. The sample was heated at 20 °C/min to 400 °C, held at 400 °C for 240 min, and heated to 900 °C at 20 °C/min.

of condensation (Table 3).⁴⁵ In addition, the integrity of the carbon–silicon bond during sol–gel polymerization and processing was confirmed by the absence of Q resonances in the ^{29}Si SSNMR.⁴⁶

Bulk physical properties of the materials were probed. Since many bridged polysilsesquioxanes are porous,⁷ the surface area of the xerogels was determined. The results revealed that **4a–e** displayed type II isotherms⁴⁷ and were uniformly nonporous (1.0 – 2.0 m^2/g) by N_2 sorption porosimetry.

The transparent xerogels exhibited a UV/vis absorption below 360 nm. The thermal characteristics of the xerogels were obtained by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). The DSC showed a small endotherm due to loss of adsorbed solvent or further condensation at ~ 100 °C. The materials were stable until an exotherm at 500–520 °C indicative of decomposition. Both isothermal and temperature gradient TGA were performed and indicated the thermal stability of the polysilsesquioxanes (Table 4). The thermal stability of these materials at 400 °C is indicated by isothermal TGA trace (Figure 3). After this extended heating, the clear and colorless thick films darkened but remained transparent and became more brittle.

The thermal stability of xerogels **4a–d** are comparable with analogous linear polyimides.⁴⁸ For example, in analogy with x-BPTDI **4b**, a polyimide made with

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(41) Although only 3 equiv of water is theoretically necessary for complete condensation, addition of less than 6 equiv of water extends the gel time from 3 h (6 equivalent H_2O), to 2 days (4.5 equiv H_2O) to >3 weeks (3 equiv of H_2O). Horne, D.; Hobson, S. T.; Shea, K. J., unpublished results. Similar results have been reported for the condensation of $\text{Si}(\text{OEt})_4$; see: Klien, L. K. *Annu. Rev. Mater. Sci.* **1985**, *15*, 227.

(42) The thickness of films prepared under similar conditions have been measured by ellipsometry. See ref 17.

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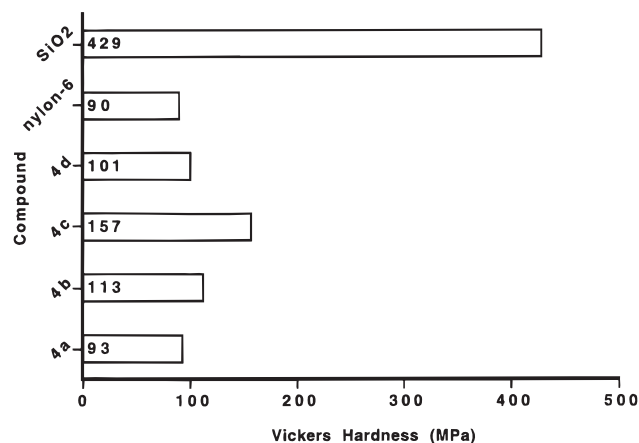


Figure 4 Hardness of polysilsesquioxanes and reference materials.

diphenyltetracarboxylic dianhydride and an aromatic diamine showed a weight loss of 1.4% after 3 h at 450 °C under helium.⁴⁸

The hardness of dried xerogels was studied using a Buehler microhardness tester using a Vickers diamond indenter.⁴⁹ The microhardness was measured by mounting a small (5 × 5 mm) piece of dried xerogel in phenol resin (180 °C, 2800 psi, 2 min), and polishing the xerogel⁵⁰ to an optical finish. A range between nylon-6 (90 MPa)⁵¹ and SiO₂ (from TEOS using HCl catalyst) (429 MPa)⁵² was obtained for the xerogels studied (Figure 4).

In addition to the hardness determination, we attempted to measure the fracture toughness of the

materials, but in contrast to amorphous glass that fractures under 1 kg force,⁵³ even under high test loads (> 20 kg), no cracks were apparent.

Conclusion

New hybrid organic–inorganic materials were synthesized by the sol–gel polymerization of bis(triethoxysilyl)imide monomers. Monomers **3a–d** were synthesized by transimidation of 2-(aminopyridyl)imides. The synthesis avoids the release of water and gave analytically pure monomers in reasonable yield. Polymerizations occurred at ambient temperature in THF rapidly under acidic (HCl) conditions. The resulting materials were solvent processed or allowed to slowly air-dry to give transparent or translucent xerogels. Thin films were cast at ambient temperatures and later cured under moderate temperatures (100 °C). Bridged bisimide polysilsesquioxanes displayed a decomposition temperature between 500 and 520 °C and showed only minimal weight loss (0.2–1.4%) after 4 h at 400 °C under N₂. These materials contained between 16 and 10% SiO₂ and exhibited hardness values intermediate between an organic polymer and pure silica.

Further investigation into the mechanical and surface properties of this materials is anticipated to probe their application to either optical or electronic applications.

Acknowledgment. The authors thank Mr. Robert Perez and Professor Enrique Lavernia of the UCI Department of Chemical and Biological Engineering for assistance with the Buehler Microhardness tester. We gratefully acknowledge the Division of Materials Research, National Science Foundation for financial support. We also thank Dr. Jeff Wengrovius, Corporate Research, General Electric for providing us with several samples of bisanhydrides.

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