Nonshrinking, Photopolymerizable Polycarbosiloxanes through Ring-Opening Polymerization of Disilaoxacyclopentane Monomers

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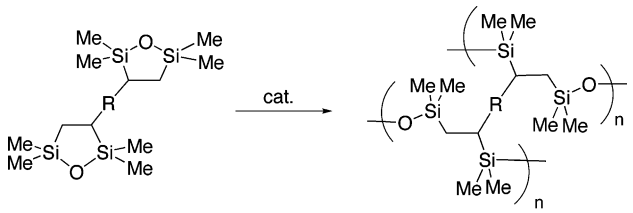
Shrinkage during polymerization and processing of silica and hybrid organic−inorganic xerogels prohibits net-shape fabrication and introduces stresses that often result in cracking. In this study, we have used a new class of hybrid organic−inorganic monomers based on the ring-opening polymerization of two strained disilaoxacyclopentyl groups bridged by alkylene or arylene groups to control the physical and mechanical properties of the resulting monolithic gels. Shrinkage is virtually eliminated by the ring-opening polymerization chemistry which, in contrast to that of alkoxysilane sol−gels, does not require water or solvent, or produce any condensation byproducts. The bridging group can be varied in length and flexibility and the bridged monomers can be copolymerized with the monomer 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane, to permit molecular engineering of the glass transition temperature (T_g) and coefficient of thermal expansion in the resulting hybrid materials. Most importantly, we have demonstrated for the first time that the ring-opening polymerizations of disilaoxacyclopentane monomers can be performed using Brønsted acid catalysts. This has also enabled the use of photoacid generators to fabricate thin films and bulk samples of these hybrid materials.

Introduction

Brønsted base- or acid-catalyzed ring-opening polymerization (ROP) of disilaoxacyclopentanes is a new, solvent-free alternative to sol−gel processing of highly cross-linked, hybrid organic−inorganic materials (Scheme 1).[1−7]

Sol−gel polymerization of tetraalkoxysilanes suffers considerable shrinkage from the net replacement of four alkoxide groups with two siloxane bonds per monomer repeat unit in the fully condensed silica gel, as well as the loss of the alkoxide groups themselves.[8,9] This, coupled with the requirement of an alcohol or ethereal solvent to mix the hydrophobic monomer with two or more equivalents of water, leads to shrinkages of up to 95% during the air-drying of gels to afford xerogels. Shrinkage can be reduced by supercritical drying to afford porous aerogels or by performing "solvent-free" polymerizations with mixtures of tetralkoxysilane, water, and catalyst to prepare porous xerogels.[10−12] An even more elegant strategy uses monomers with the alkoxide groups modified to be polymerizable by either free radical or rin-opening metathesis polymerization chemistry.[13−20] This prevents shrinkage due to loss of volatile organic constituents, but does not compensate for shrinkage

Scheme 1. Ring-Opening Polymerization of Bridged Disilaoxacyclopentanes (R = 1,4-phenylene (2), 1,4-butylene (3)) to Afford Polycarboxosiloxane Gels with Four Bonds to Every Monomer Repeat Unit



R = 1,4-Phenylene (**2**),
R = *n*-Butylene (**3**)

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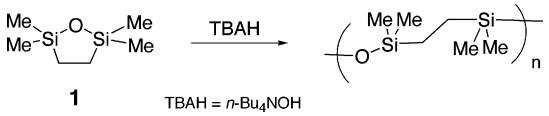
Scheme 2. Base-Catalyzed Ring-Opening Polymerization of 2,2,5,5-Tetramethyldisila-1-oxacyclopentane



that comes from conversion of nonbonding distances between monomers to the higher densities arising from covalent linkages between monomers.

One well-proven strategy for reducing shrinkage associated with the preparation of organic polymers is ring-opening polymerization of cyclic monomers such as epoxides,[21,22] spirocarbonates,[23,24] and cyclic ethers.[25] Ring strain provides the thermodynamic driving force, the chain growth mechanism eliminates co-reactants (such as water), solvents, and condensation products, and the ring-opened structure compensates for the volumetric losses resulting from the polymerization. The base-catalyzed, solvent-free, ring-opening polymerization of the strained (12 kcal/mol)[26,27] tetramethyldisilaoxacyclopentane (**1**) occurred with less than 5% loss of volume (Scheme 2).[28] Unfortunately, the products of the polymerization of this colorless liquid monomer are oils or tacky solids with T_g values comparable to that of poly(dimethylsiloxane).

In this study, two of the tetramethyldisilaoxacyclopentyl groups were linked together with organic bridging groups resulting in monomers whose polymerization would afford a highly cross-linked polymer that, like silica gels, possesses up to four possible siloxane bonds to each repeat unit (Scheme 1) and would be expected to have a much higher T_g. Monomers with a rigid 1,4-phenylene bridge (**2**) or a flexible 1,4-butylene bridge (**3**) were designed and synthesized to gauge the influence of molecular level perturbations on the thermomechanical properties of the resulting, highly cross-linked materials. The variability of the bridging group is also invaluable in preparing a monomer that is liquid at room temperature and pressure, a prerequisite to performing solvent free ROPs. Ring opening polymerization of disilaoxacyclopentane monomers was previously shown to be catalyzed by base catalysts, but not by Lewis acids.[26,27] As the lack of suitable photobase generators has restricted most photolithographic processes to acid-catalyzed reactions,[29] Brønsted acids, including photoacid generators, were examined as polymerization catalysts for the ring-opening polymerizations for monomers **1**−**3**.

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Experimental Section

All reactions were performed under an inert atmosphere of argon unless indicated otherwise. Diethynylbenzene was purchased from TCI America and used as received. 1,7-Octadiyne was purchased from GFS and used as received. 1,1,2,2-Tetramethyl-1,2-dimethoxydisilane was synthesized according to published reports.[1] UV9310C photoacid generator was obtained from GS Silicones and used as received. 2,2,5,5-Tetramethyl-2,5-disila-1-oxacyclopentane was obtained from Gelest and used as received. All other reagents were purchased from Aldrich Chemicals Co. and used as received. Solution NMR spectra were performed on a Bruker DRX400 spectrometer (^{1}H, 400.2 MHz; ^{13}C 100.0 MHz; ^{29}Si, 80.0 MHz) and were referenced against residual solvent peaks or external TMS. Solid state ^{13}C and ^{29}Si CP MAS NMR spectra were obtained with a Bruker AMX-400 MHz spectrometer at 100.6 and 79.5 MHz, respectively, and were acquired with magic angle spinning (MAS) speeds of ∼5 kHz and ∼3−5 kHz, respectively. ^{13}C NMR spectra were acquired using cross polarization (CP) with a relaxation delay of 1 s and a cross polarization time of 2 ms. ^{13}C NMR referencing was performed on the carbonyl resonance of solid glycine (δ = 176.0). ^{29}Si NMR spectra were acquired using single pulse excitation with a relaxation delay of 480 s. With ^{29}Si T_1 values ranging from 19 to 135 s, the relaxation delay is ≥3 T_1 which is sufficient for quantitative interpretation of spectra. ^{29}Si CP MAS NMR spectra were deconvoluted using a Lorentz−Gaussian (50:50) fit. Infrared spectra were obtained on a Perkin-Elmer 1750 Fourier transform infrared spectrophotometer. Glass transition and coefficient of thermal expansion measurements were made on a Perkin-Elmer DMA7 instrument.

Synthesis of 4. A solution of diethynylbenzene (5.00 g, 0.040 mol), $Me_4Si_2(OMe)_2$ (21.00 g, 0.12 mol), and $(Ph_3P)_4Pd$ (0.46 g, 3.98×10^{-4} mol) in toluene (50 mL) was heated at 110 °C for 12 h. The volatiles were distilled at ambient pressure to leave a black solid residue. The product was sublimed under vacuum (100 °C, 0.01 mmHg) to give a white solid, mp = 137 °C (16.4 g, 85% yield). IR for **4**: 2955.3, 1489.2, 1252.2, 931.5, 826.2, 637.2 cm^{-1}. NMR for **4**: ^{1}H (400.1 MHz, C_6D_6), δ 7.17 (s, 4H), 6.79 (s, 2H), 3.36 (s, 6H), 3.18 (s, 6H), 0.39 (s, 12H), 0.25 (s, 12H); ^{13}C (100.05 MHz, C_6D_6), δ 162.7, 147.9, 146.5, 126.9, 50.0, 49.5, −0.5, −0.7; ^{29}Si (80.5 MHz, C_6D_6), δ 15.7, 14.2. LRMS (CI methane): *m*/*z* 483 $[M + H]^+$, 391 $[M - 2CH_3 - 2CH_3O]^+$, 375 $[M - 2CH_3 - 2CH_3O - O]^+$.

Synthesis of 5. To a solution of **4** (6.00 g, 0.012 mol) in CH_2Cl_2 (50 mL) was added 0.62 mL of 0.1 N aqueous HCl solution. The mixture was stirred for 2 h at room temperature, after which the volatiles were removed in vacuo (RT, 0.01 Torr). The product was then redissolved in CH_2Cl_2 (50 mL) and stirred over activated 4-Å molecular sieves overnight. The sieves were then filtered and the volatiles were removed to leave analytically pure **5** as a white solid, mp = 148 °C (4.68 g, 100% yield). IR for **5**: 2955.1, 1489.0, 1251.9, 931.8, 826.3, 786.7, 637.2 cm^{-1}. NMR for **5**: ^{1}H (400.1 MHz, C_6D_6), δ 7.47 (s, 4H), 7.20 (s, 2H), 0.41 (s, 12H), 0.28 (s, 12H); ^{13}C (100.05 MHz, C_6D_6), δ 164.6, 144.7, 140.3, 127.1, 1.5, 1.0; ^{29}Si (80.5 MHz, C_6D_6), δ 15.2, 13.7. LRMS (CI methane): *m*/*z* = 391 $[M + H]^+$, 375 $[M - O]^+$.

Synthesis of 2. A solution of **5** (5.00 g, 0.0128 mol) in CH_2Cl_2 was placed under an atmosphere of H_2 (40 psi) with Pd/C (10% Pd content, 1.0 mol %) and stirred for 48 h. The insolubles were filtered through Celite and the volatiles were removed in vacuo (RT, 0.01 mmHg) to leave analytically pure **2** as a white solid, mp 112 °C (5.05 g, 100% yield). IR for **2**: 2957.8, 2912.8, 1654.8, 1506.5, 1420.2, 1254.4, 1144.4, 1030.9, 920.7, 854.4, 657.9, 623.4 cm^{-1}. NMR for **2**: ^{1}H (400.1 MHz, C_6D_6), δ 7.10 (s, 4H), 2.48 (t, 2H), 1.16 (d, 4H), 0.26 (s, 6H), 0.25 (s, 6H), 0.14 (s, 6H), −0.09 (s, 6H); ^{13}C (100.05 MHz, C_6D_6), δ 140.6, 126.6, 32.8, 17.0, 0.9,

0.4, −0.3, −2.5; ^{29}Si (80.5 MHz, C_6D_6), δ 21.9, 20.9. LRMS (CI methane): *m/z* 395 $[M + H]^+$, 379 $[M - O]^+$.

Synthesis of 6. A mixture of 1,7-octadiyne (5.00 g, 40.0 mmol), $Me_4Si_2(OMe)_2$ (21.00 g, 120 mmol), and $(Ph_3P)_4Pd$ (0.46 g, 3.98×10^{-4} mol) was heated at reflux temperature for 12 h. The volatiles were distilled at ambient pressure and the product was distilled under vacuum to leave analytically pure **6**, bp = 135−140 °C (60 mmHg). IR for **6**: 2955.3, 1489.2, 1252.2, 931.5, 826.2, 637.2 cm^{-1}. NMR for **6**: ^{1}H (400.1 MHz, C_6D_6), δ 7.17 (s, 4H), 6.79 (s, 2H), 3.36 (s, 6H), 3.18 (s, 6H), 0.39 (s, 12H), 0.25 (s, 12H); ^{13}C (100.05 MHz, C_6D_6), δ 162.7, 147.9, 146.5, 126.9, 50.0, 49.5, −0.5, −0.7; ^{29}Si (80.5 MHz, C_6D_6), δ 15.7, 14.2. LRMS (CI methane): *m/z* 483 $[M + H]^+$, 391 $[M - 2CH_3 - 2CH_3O]^+$, 375 $[M - 2CH_3 - 2CH_3O - O].^+$

Synthesis of 7. To a solution of **6** (6.00 g, 12 mmol) in CH_2Cl_2 (50 mL) was added 0.43 mL of 0.1 N aqueous HCl solution (24 mmol H_2O). The mixture was stirred for 2 h at room temperature, after which the volatiles were removed in vacuo (RT, 0.01 mmHg). The product was then redissolved in CH_2Cl_2 (50 mL) and stirred over activated 4-Å molecular sieves overnight. The sieves were then filtered and the volatiles were removed to leave analytically pure **7** as a slightly yellow liquid (100% yield). IR for **7**: 2957, 1527, 1406, 1252, 1055, 928, 882, 852, 785, 659 cm^{-1}. NMR for **7**: ^{1}H (400.1 MHz, C_6D_6), δ 6.59 (s, 2H), 2.30 (br. m, 4H), 1.48 (br. m., 4H), 0.25 (s, 12H), 0.23 (s, 12H); ^{13}C (100.05 MHz, C_6D_6), δ 169.1, 144.0, 36.5, 28.8, 1.1, 0.7; ^{29}Si (80.5 MHz, C_6D_6), δ 14.0, 13.2. LRMS (CI methane): *m/z* 391 $[M + H]^+$, 375 $[M - O]^+$.

Synthesis of 3. A solution of **7** (5.00 g, 0.0128 mol) in CH_2Cl_2 was placed under an atmosphere of H_2 (5.4 MPa) with Pd/C (10% Pd content, 1.0 mol %) and stirred for 24 h. The insolubles were filtered off with Celite and the volatiles were removed in vacuo (RT, 0.01 mmHg) to leave analytically pure **3** as a slightly yellow oil (100% yield). IR for **3**: 2957, 2916, 2850, 1407, 1252, 1057, 922, 876, 849, 796 cm^{-1}. NMR for **3**: ^{1}H (400.1 MHz, C_6D_6), δ 1.49−0.90 (br. m., 8H), 0.45 (br. m., 2H), 0.25 (s, 6H), 0.20 (s, 6H), 0.13 (s, 6H), 0.11 (s, 6H), the cyclic C*H*$_2$'s over lap with C*H*$_3$'s and are not assigned; ^{13}C (100.05 MHz, C_6D_6), δ 34.1, 34.0, 30.7, 30.6, 25.0, 18.6, 18.5, 1.1, 0.8, 0.7, 0.6, −2.6; ^{29}Si (80.5 MHz, C_6D_6), δ 23.2, 21.3. LRMS (CI methane): *m/z* 395 $[M + H]^+$, 379 $[M - O]^+$.

Polymerization Reactions. Polymerizations were performed, neat, with either monomer **2** or **3** or as a copolymer system with **1** by adding 0.50 mol % of *n*-Bu_4NOH (based on **2** or **3**) to the monomer and stirring for 1 min. The solutions were then allowed to stand until they gelled (approximately 30 min). The gels were analyzed by solid-state NMR spectroscopy. Thermal properties data (T_g and CTE) are tabulated in the text. All polymers give a signature single resonance at 8.5 ppm in the solid state ^{29}Si NMR spectrum. The extent of reaction, independent of composition, is 100% or all polymerization reactions, based on NMR spectroscopy, as no monomer resonances are observed in ^{13}C and ^{29}Si NMR spectra of the final materials.

Polymerization of 2. To a 1 M solution of **2** in THF (1.971 g, 5.00 mL solution) was added TBAH (10 μL of 1 M solution in methanol/toluene, 0.20 mol %) and vigorously stirred. The solution was allowed to stand overnight during which time it formed an immobile gel. The contents were crushed and dried in vacuo (RT, 0.01 Torr) to remove volatiles and leave a white solid. IR for polymer: 2958.0, 1509.3, 1419.9, 1295.9, 1061.8, 840.4, 784.9, 532.8 cm^{-1}. ^{13}C CP MAS NMR: δ 139.9, 129.1, 31.6, 18.0, 0.4. ^{29}Si CP MAS NMR: δ 9.8, 5.5. TGA showed two weight loss transitions, 350 °C (19%) and 500 °C (64%). Ceramic residue left was 17.1%. Elemental analysis calcd. for $C_{18}H_{34}O_2Si_4$: C, 54.76%; H, 8.68%; Si, 28.64%. Found: C, 53.03%l H, 9.21%. Si, 27.84%.

Copolymerization of 2 with 1. An 80:20 ratio (by weight, 1.00 g total) solution of **1:2** was made and TBAH (10 μL of 1 M solution in methanol/toluene, 0.20 mol % based on **2**) was added with vigorous stirring. Within 30 s, the solution solidified into a nonflowing gel. ^{13}C CPMAS NMR: δ 140.1, 127.9, 31.7, 17.4, 9.9, −0.1. ^{29}Si CPMAS NMR: δ 8.6, 5.3. TGA showed one weight loss transition at 500 °C (98%). Elemental analysis calcd. for polymer: C, 46.90%; H, 9.78%; Si, 33.72%. Found: C, 46.21%; H, 10.37%; Si, 30.06%.

Polymerization of 3. To neat **3**, 0.5 mol % of TBAH was added. The mixture solidified into an insoluble material after approximately 30 min. It was analyzed by solid-state NMR spectroscopy. In the solid state ^{13}C NMR spectrum, the homopolymer of **3** displays two broad resonances at 30.6 and 20.2 ppm and two sharp signals at 1.5 and −0.4 ppm. The solid state ^{29}Si NMR spectrum displays one broad signal centered at 8.5 ppm.

Copolymerization Reactions of 3. All copolymerizations were performed in a similar manner. In a typical reaction, the appropriate amount of the bridged disilaoxacyclopentane was mixed with 2,2,5,5-tetramethyl-2,5-disila-1-oxacyclopentane under neat conditions (ratios shown in Table 2) to obtain a homogeneous solution, to which was added 0.5 mol % TBAH catalyst (based on the bridged complex). Generally, mixtures gelled within 30 min after initial mixing. Samples were analyzed to measure glass transition temperature (T_g) and coefficient of thermal expansion (CTE), results of which are shown in Table 2. All copolymers display sharp resonances at 32.5, 30.0, 21.4, 17.2, 9.7, 1.4, and −0.3 ppm in the ^{13}C NMR spectrum. The ratio of the resonances at 1.4 and −0.3 ppm (due to linear component) to the rest of the spectrum changes depending on the amount of linear component present in the polymer. All polymers give a signature, single broad resonance, centered at 8.5 ppm in the solid state ^{29}Si spectrum.

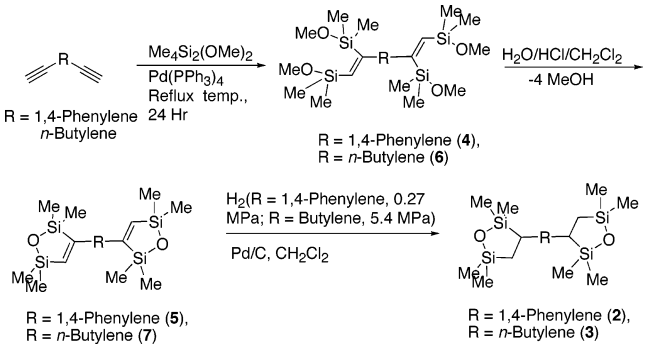
Polymerization with Brønsted Acid. In a typical reaction, 0.5 mol % of formic acid was added to the monomer, and the mixture was allowed to stand until it solidified, taking approximately 30 min to occur. All resulting polymers were analyzed by solid state ^{29}Si NMR spectroscopy. The resulting polymers displayed resonances identical to those obtained with TBAH as catalyst.

Polymerization with Photoacid Generators. In a typical reaction, either UV9310 (obtained from GE Silicones) or $Ph_2I^{2-}(^-O_3SCF_3)$ was added (0.2 mol % based on bridged complex) to the monomer mixture under neat conditions and exposed to short UV light for 1 min. After letting the mixture sit for approximately 30 min, it solidified. The solid material was analyzed by solid state ^{29}Si NMR spectroscopy which displayed resonances identical to those obtained with TBAH as catalyst.

Results

Insertion of a bridging organic group between two disilaoxacyclopentyl groups was designed to yield monomers whose polymerization would afford hybrid organic−inorganic materials with tailorable thermomechanical properties. One drawback is that the increase in mass or inherent crystallizability due to the organic bridging group could result in a solid monomer unsuitable for direct polymerization. In fact, we discovered that the monomer with the rigid 1,4-phenylene bridging group (**2**) was a crystalline solid, despite the disorder imparted by the two disilaoxacyclopentyl groups, thus it requires monomer **1** as a solvent and comonomer for nonshrinking polymerizations. Fortunately, the butylene-bridging group was sufficiently flexible to result in a liquid monomer (**3**) that could be polymerized by itself or with

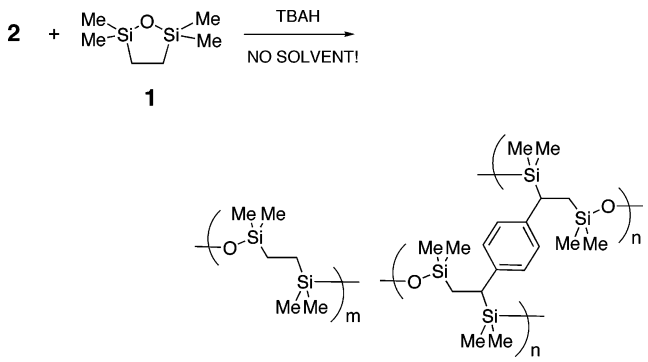
Scheme 3. Synthesis of Monomers 2 and 3 by the Palladium-Catalyzed Disilylation of 1,7-Octadiyne, Hydrolysis and Cyclization, and Hydrogenation



monomer **1**. The phenylene (**2**) and butylene (**3**) bridged monomers were prepared in three steps from diethynylbenzene and 1,7-octadiyne (Scheme 3), respectively. The tetrakis(dimethylmethoxysilyl) functionalized intermediates, obtained from the disilylation of the diynes, were cyclized through acid-catalyzed hydrolysis before hydrogenation to provide the highest yield ring closure. Attempts to ROP the unsaturated intermediates (**5** and **7**) were unsuccessful likely due to the entropic costs posed by the conformational constraints imposed by the carbon−carbon double bond on the ring opening polymerization. Hydrogenation to afford the butylene-bridged monomer required significantly greater pressure hydrogen (5.4 MPa) than the reduction of the phenylene-bridged intermediate (0.27 MPa).

Polymer Synthesis. Polymerization of monomers **2** and **3** proved to be unaffected by the presence of the organic bridging groups. The first representatives of this new class of hybrid materials were prepared from the ROP of the *p*-phenylene-bridged disilaoxacyclopentane monomer, **2**, dissolved in THF catalyzed with tetrabutylammonium hydroxide (TBAH).[1] Because monomer **2** is a solid, its homopolymerization must be performed in a solvent or in the melt (mp = 112 °C). The melt polymerizations were too fast and vigorous, and polymerization in THF, while convenient, negated ring-opening polymerization's advantage for eliminating shrinkage due to the evaporation of the solvent. However, by using **1** as a reactive comonomer and solvent (Scheme 4) it was possible to prepare polymers with minimal shrinkage. As a liquid at room temperature (bp = 150 °C at 60 mmHg), monomer **3** was readily homopolymerized without solvent. Polymerizations of all of the monomers were exothermic resulting in temperature increases to over 45 °C during the polymerization reactions. Interestingly, the homo- and copolymerizations of **3** were slower and less exothermic than the copolymerization of **2**, approximately 30 min compared to about 1 min for copolymerization of **2**. The resulting polymers were transparent, light yellow gels. Polymers of **2** and **3** did not dissolve in organic solvents or water (no swelling). The homopolymer of **2** and its copolymers with **1** are transparent, brittle materials and the copolymer of **2**/**1** does not display any visual evidence of shrinkage (5.00 mL of monomer and catalyst were added to a graduated cylinder and allowed to polymerize; no change in volume was observed after polymerization). Complete encapsulation of microelectronic

Scheme 4. Copolymerization of Phenylene-Bridged Monomer 2 with Comonomer 1 Which Serves as Monomer and Solvent[a]



[a] Monomer **1** forms linear, flexible segments in the resulting coplymers that lower the glass transition temperature and increase the coefficient of thermal expansion.

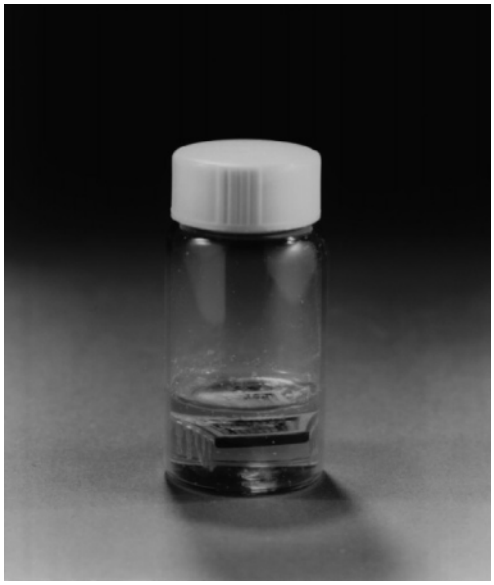


Figure 1. Microelectronic test chip encapsulated with a nonporous hybrid organic−inorganic gel prepared by the ring-opening polymerization of phenylene-bridged monomer **1** with monomer **3**.

devices was performed by pre-polymerizing a base or foundation of the bridged polymer then embedding the device with a second polymerization reaction (Figure 1).

In contrast to earlier reports that disilaoxacyclopentane monomers would only polymerize with base catalysts,[26,27] we discovered that Brønsted acids polymerized monomers **1**−**3** with ease. For example, triflic acid and formic acid were found to effectively catalyze the copolymerization of **2** with **1** or homopolymerization of **3**. Furthermore, photoacid generators (PAG) such as $Ph_2I^{2-}(^{-}O_3SCF_3)$ and UV9310C (available from GE-Silicones) were also used to catalyze the ROP by exposing a solution of the disilaoxacyclopentane monomers with the PAG to shortwave ultraviolet light, for several seconds to activate the PAG, and allowing the solution to react.

Characterization of Polymers. Because the polymers were highly cross-linked and insoluble, the intractable materials were structurally characterized by solid state ^{13}C and ^{29}Si NMR spectroscopy. Homopolymer of **3** displays

Table 1. Effect of Bridging Group on the Glass Transition Temperature (T_g) and Coefficient of Thermal Expansion (CTE) of Gels

bridging group	T_g (°C)	CTE (e^{-6}/°C)
p-phenylene	80.0	110
n-butylene	−33.5	227

Table 2. Effect of Linear Structure from the Copolymerization with Varying Quantities of 1 with the Phenylene- and Butylene-Bridged Monomers on Thermal Properties of Copolymeric Gels

copolymer mix ratio (by weight, bridge:linear)	T_g (°C)	CTE (e^{-6}/°C)
phenylene bridged, 1:9	−81	352
phenylene bridged, 1:4	−74	302
butylene bridged, 1:3	∼ −82	268
butylene bridged, 1:1	−69	244
butylene bridged, 3:1	−53	236

four resonances in the ^{13}C NMR: two broad resonances at 30.6 and 20.2 ppm and two sharp signals at 1.5 and −0.4 ppm. Copolymers of **3** with **1** all display resonances at 32.5, 30.0, 21.4, 17.2, 9.7, 1.4, −0.3 ppm. The ratio of the resonances at 1.4 and −0.3 ppm to the rest of the spectrum changes depending on the amount of **1** present in the polymer. In the ^{29}Si NMR, all of the polymers made with **3** display only one broad resonance centered at 8.5 ppm. Because the ^{29}Si resonances of the unreacted monomer, **3**, are downfield by about 15 ppm (it displays two resonances of equal intensity at 23.2 and 21.3 ppm) from the analogous acyclic or ring-opened form, solid state ^{29}Si NMR could easily be used to show that the strained disilaoxacyclopentane group is completely consumed during the chain growth polymerization.

The thermomechanical properties of the polymers were characterized to ascertain the utility of these materials as encapsulants or coatings. In general, all the polymers made with **3** were brittle, rubbery materials which increased in rubbery character as the amount of linear component **1** increased. On the other hand, the homopolymer of **1**, once all of the solvent was removed, was a glassy material. The glass transition temperature, determined using differential mechanical analyses, revealed that the T_g was readily controlled through the nature of the bridging group or the amount of **1** used as comonomer. The homopolymer of **3** has a T_g of −33.5 °C, whereas homopolymer of **2** has a much higher T_g of 80 °C (Table 1). The drop in glass transition temperature with the substitution of a rigid segment, such as the phenylene bridge in **2**, with a relatively flexible one, such as the butylene bridge in **2**, is expected[30] and demonstrates the versatility of this approach to engineering the mechanical properties of these materials. The coefficient of thermal expansion (CTE) of the homopolymer of **3** is significantly greater than that of **2**.

Copolymerizing **2** and **3** with the linear monomer **1** provides an easy route to more flexible materials. For example, when the linear comonomer **1** is used with the phenylene-bridged disilaoxacyclopentane **2**, the T_g of the final material decreases dramatically to approximately −80 °C. Increasing the amount of **1** lowers the T_g and increases the CTE of the final material (Table 2). However, since **2** is a solid precursor, it has a solubility limit of about 25% (by weight) in **1**. Solubility is not a limiting factor when using the butylene-bridged precursor, **3**, since it is a liquid. One can easily vary the amount of the bridging component in the mixture from minor to major component of the final materials (Table 2). For example, one can vary the amount of the bridging component **3** from 25% to 75% (by weight) in the final material. Plots of ratio of the cross-linking component versus the T_g and CTE are shown in Figures 2 and 3, respectively, which display a relatively linear relationship. Thus, one can easily choose the appropriate amount of the cross-linking component for a specific application by referring to the plot.

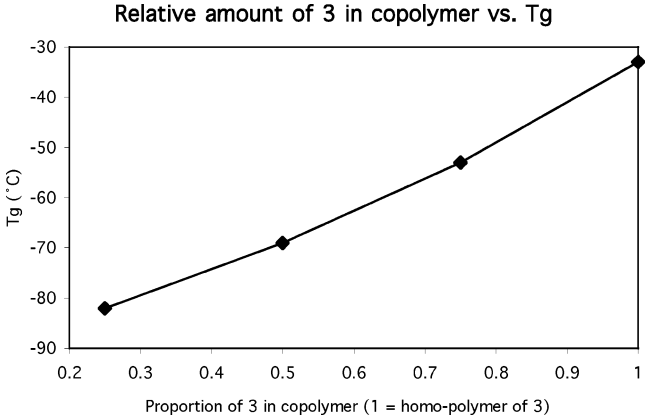


Figure 2. Influence of the quantity of **3** in copolymer with **1** on glass transition temperature, T_g.

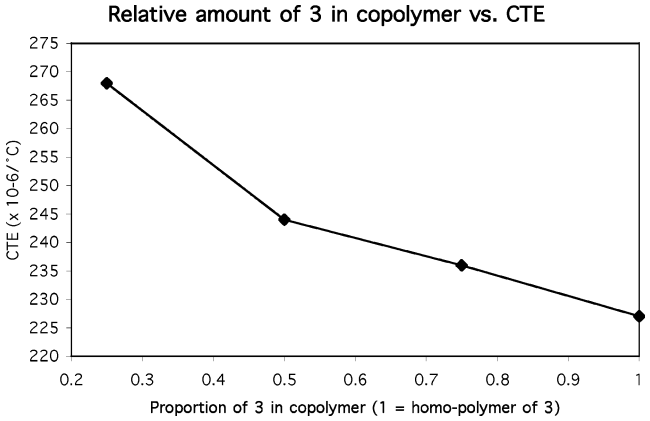


Figure 3. Plot of change in polymer CTE with increasing **3** in copolymer with **1**.

Conclusions

Ring-opening polymerization of bridged disilaoxacyclopentanes, **2**−**3**, has been demonstrated to afford highly cross-linked, hybrid organic−inorganic materials. The polymerizations, requiring only a basic or Brønsted acid catalyst, as well as photoacid generators, and no water or solvent, are a nonshrinking alternative to traditional sol−gel polymerizations containing high levels of siloxane bonding. Unlike sol−gels prepared from alkoxysilanes polymerizations, these materials are nonporous and suitable for encapsulations. Our discovery that the monomers would polymerize with photoacids opens up the possibility of patterning coatings of the nonporous hybrids on surfaces. The tetrafunctionality of the monomers significantly improves the thermomechanical properties over the linear polymer derived from the parent

(30) Sokolova, L. V. *Russ. Polym. News* **2002**, *7*, 19−33.

disilaoxacyclopentane monomer, **1**. We have also demonstrated that the nature of the bridging group or the ratio with disilaoxacyclopentane, **1**, can be used to control rate of polymerization and engineer the glass transition temperature and thermal expansion coefficient. This degree of control coupled with the lack of porosity measured makes these materials excellent candidates for membranes as well, which we are currently pursuing.

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