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Synthesis and Properties of Hybrid Organic−Inorganic Materials Containing Covalently Bonded Luminescent Polygermanes

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Covalent binding of arylmethylpolygermanes into hybrid silica materials leads to substantial increases in thermal stability without degrading Ge−Ge σ-conjugation, as determined by UV−vis absorption and fluorescent emission spectroscopy. Poly(methyltrimethoxysilylphenylgermane) was prepared by ruthenium-catalyzed demethanative coupling of dimethyl(trimethoxysilylphenyl)germane, and then hydrolyzed and cured in the presence of either tetraethoxysilane (TEOS) or β-acetoxyethylsilsesquioxane (BAESSQ) to yield hybrid materials containing the polygermane linked to the matrix at every repeat unit. Thermal stability of the bulk hybrid materials was examined by TGA, and films were examined by UV−vis spectroscopy following thermal treatment and photochemical irradiation. Conjugation of the Ge−Ge chains is maintained to 380 °C under nitrogen in the case of the BAESSQ-derived hybrids, but only 200 °C in air. The photolytic stability of the hybrid films is greater than the parent poly(methylphenylgermane), but the gains are less dramatic. A model is proposed in which anchoring each germanium in the polymer chain to the silica matrix reduces mobility of germyl radicals produced by both thermolysis and photolysis, leading to efficient recombination to restore the Ge−Ge chains under nitrogen. On the other hand, germylene intermediates generated only during photolysis are more reactive and can combine irreversibly with Si−O−Si bonds or residual SiOH groups in the silica matrix, leading to faster photolytic degradation of the conjugated Ge−Ge chains, even under nitrogen.

Introduction

The polymers of heavier group 14 elements—polysilanes, polygermanes, and polystannanes—exhibit interesting optical and electronic properties due to the extensive delocalization of σ-electrons along the polymer backbone.[1−4] Although these simple polymers are potentially attractive materials for several commercial applications, instability to prolonged exposure to light or elevated temperatures limits their use.

The thermal decomposition of polysilanes occurs primarily by homolytic scission and formation of smaller cyclic polysilanes.[5−7] However, polysilanes and polygermanes are also light sensitive,[1,8−13] especially in the presence of oxygen.[13,14] Photolytic degradation of these polymers has been shown to involve two main paths: homolytic cleavage of Si−Si or Ge−Ge bonds and extrusion of the divalent silylene or germylene.[10,12]

One approach to improving thermal and photochemical stability of thin films of such polymers involves their encapsulation and immobilization in an inert inorganic matrix such as silica. The simplest method is to merely physically trap the polymer chains by creating the matrix by sol−gel condensation in the presence of an unmodified polysilane. This, however, gives little control over polymer aggregation and the mobility of fragments produced during degradation. A greater degree of immobilization is obtained when the polymer is covalently linked to the matrix, an approach that usually requires incorporation of hydrolyzable alkoxysilyl substituents.

Inoue, Matsukawa, and co-workers recently described hybrid polysilanes containing short lengths of trimethoxysilyl-substituted acrylates inserted into preformed polysilane chains.[15,16] Subsequent sol−gel condensation in the presence of tetraethoxysilane (TEOS) led to hybrid materials that did exhibit a modest increase in stability to UV irradiation. However, the relatively low density of connections between the polymer and silica matrix does not provide complete immobilization, especially as chain scission progresses and the polysilane detaches from the polyacrylate cross-linking

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sites. Optimum immobilization and encapsulation of the electronically active Si−Si backbone requires cross-linking sites (e.g., trialkoxysilyl groups) on each repeat unit of the chain. Unfortunately, the harsh conditions typically used to synthesize polysilanes are not compatible with such substituents.

We recently described the synthesis of substituted polymethylarylgermanes by the demethanative coupling of aryldimethylgermane monomers using ruthenium catalysts.[17,18] This method gives moderate to high yields of polygermanes, and importantly, is compatible with many functional groups which are not stable to the traditional Wurtz coupling route. Although it has not proved feasible to extend the demethanative polymerization to silicon compounds, it is well-established that polygermanes exhibit electronic and optical properties that are very similar to those of interest in the polysilanes.[12,19−21]

We now report the application of demethanative coupling to the synthesis of poly(methyltrimethoxysilylphenylgermane) (PMSG), a σ-conjugated polymer containing hydrolyzable cross-linking sites attached to each repeat unit of the chain. Hybrid polygermane/silica films have been prepared using two different condensation methods, and the thermal- and UV-stability of these new materials have been determined.

Experimental Section

The syntheses of the monomer, dimethyl(trimethoxysilylphenyl)germane, and polymer, poly(methyltrimethoxysilylphenylgermane) (PMSG), were carried out in dried glassware under N_2 atmosphere in a drybox or using standard Schlenk and high vacuum line techniques. Solvents were dried over Na/K benzophenone prior to use. Dimethyldichlorogermane and tetramethoxysilane were purchased from Gelest Inc. The literature procedures for preparing $(PMe_3)_4RuMe_2$ were followed.[22,23]

^1H NMR spectra were obtained on a Bruker AM-360 spectrometer at room temperature using benzene-d_6 as a solvent. Chemical shifts are reported relative to tetramethylsilane.

Quartz substrates and Si wafer were treated with 30 mL of 98% H_2SO_4 and 15 mL of 30% H_2O_2 solution for 30 min at 150 °C. The substrates were then washed with deionized water and dried at 150 °C. Films were made by spin-casting using a Headway Research Inc. spinner. Film thicknesses were measured using a Rudolph Research Auto EI-II ellipsometer. Thermogravimetric analysis was performed on a Texas Instruments SDT 2960.

Absorption spectra were obtained using an HP8452 diode array spectrophotometer and emission spectra were measured using a Perkin-Elmer LS-50 luminescence spectrometer.

Molecular weights were determined by gel permeation chromatography, using size-exclusion columns and in-line detectors: Rainin Dynamax UV-1 absorbance detector, Wyatt Optilab 903 interferometric refractometer, and Wyatt Technology Corp. miniDAWN multiangle light scattering detector.

Thermal treatment of the thin films was carried out in a flat-bottom flask fitted with a Teflon valve adapter and heated with a heating mantle. The temperature was monitored with a thermocouple. UV irradiation was performed in a quartz tube fitted with a Teflon valve adapter using a Rayonet photochemical reactor with 254-nm low-pressure mercury lamps.

Synthesis. *p-Bromo-phenyldimethylgermane*. A 2.46 g (10.43 mmol) portion of 1,4-dibromobenzene was reacted with 0.98 equiv of *n*-butyllithium (6.40 mL, 1.6 M solution in hexane) in 45 mL of dry THF and 13 mL of dry pentane at −100 °C in a two-neck flask under N_2 for 1 h. The resulting white solution was quenched with $GeMe_2HCl$ diluted with 12 mL dry THF via a gastight syringe over 15 min. The solution changed to clear pale yellow in 20 min and was allowed to warm slowly to room temperature and stirred for 12 h. After the removal of most of the solvents, the reaction mixture was quenched with 15% NH_4Cl/H_2O solution and extracted with 100 mL of diethyl ether. The organic layer was washed 3 times with water, dried over magnesium sulfate, and filtered. Removal of the solvent in vacuo resulted in a colorless liquid that was used without further purification (86%). ^1H NMR: (δ in C_6D_6) 0.21 (d, 6 H Me-Ge), 4.44 (m, 1 H, H−Ge), 6.99 (d, 2 H, Ph), 7.30 (d, 2 H, Ph).

Dimethyl(trimethoxysilylphenyl)germane. *p*-Bromo-phenyldimethylgemane (2.276 g, 8.76 mmol) in 40 mL of dry THF and 12 mL of dry pentane was reacted with 1.1 equiv of *n*-butyllithium (6.00 mL, 1.6 M solution in hexane) at −100 °C to yield Li−Ar−$GeMe_2H$. After stirring for 1 h, 5 equiv of tetramethoxysilane (TMOS, 7.37 g, 48 mmol) in 30 mL of dry THF was pre-cooled to −100 °C and added into the reaction mixture quickly with vigorously stirring. The reaction mixture was allowed to warm slowly to room temperature and stirred for 12 h. After the solvents were removed under high vacuum, dry pet-ether (100 mL) was vacuum transferred into the flask. The clear solution was filtered under N_2 purge and solvents were removed under high vacuum to produce an opaque white liquid. Vacuum distillation yielded the desired product (1.28 g, 48%) as a colorless clear liquid. ^1H NMR (δ in C_6D_6): 0.29 (d, 6 H, Me−Ge), 3.50(s, 9 H, Me−OSi), 4.57 (m, 1 H, H−Ge), 7.48 (d, 2 H, Ph), 7.82 (d, 2 H, Ph).

Poly(methyltrimethoxysilylphenylgermane) (PMSG). A 2 mg portion of $(PMe_3)_4RuMe_2$ and 100 mg of dimethyl(trimethoxysilylphenyl)germane were loaded into a 100-mL one-neck flask in the drybox, and the mixture was stirred while protected from light. Gas evolution was observed within several minutes, and the reaction mixture solidified within 2 h. After the solidification, ca. 0.2 mL of THF was added to dissolve the polymer. After stirring for an additional 48 h, an additional 0.3 mL of THF was added, then 50 mL of dry hexane was added to precipitate the polymer. The flask was stored in a freezer (−40 °C) for 12 h to allow the full precipitation of the polymer. The precipitated polymer was collected, redissolved in THF, and then dried under high vacuum to yield 35 mg of PMSG (37% yield) as a pale yellow solid. ^1H NMR 7.82−6.92 (br) aryl, 3.5 (br) −Si(OMe), 0.50−0.4 (br) Ge−Me. GPC: $M_n = 13\,930$, $M_w = 18\,560$, $M_w/M_n = 1.3$.

Sample Preparation. *Preparation of Samples for TGA.* Solid samples of PMPG and PMSG were used without further treatment. Pure TEOS-based silica was prepared by mixing TEOS (50 mg), THF (55 mg), and 4 N HCl (14 mg) and curing the mixture for 24 h. Volatiles were removed under high vacuum at room temperature for 1 h and the white solid (~20 mg) was collected. Hybrids were prepared by adding 5 mg of PMPG or 6 mg of PMSG to the solution described above, and processed in the same manner. For the PMPG/

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TEOS hybrid, 25 mg of solid material containing ~20 wt % PMPG was collected. In the case of the PMSG/Silica (TEOS) hybrid, 27 mg containing ~22 wt % PMSG was obtained.

Hybrid Films Based on TEOS. Aliquots of 5 mg of PMSG, 50 mg of TEOS, 50 mg of ethanol, 50 mg of THF, and 20 mg of 4 N HCl were thoroughly mixed in the dark at room temperature and stirred for 1 h. Thin films were prepared by spin-casting the solution onto Si and quartz substrates at 2000 rpm for 60 s. The as-cast films thicknesses were about 420 nm, as measured by ellipsometry. The films were then heated under N_2 at 160 °C for 1 h to remove volatiles and condense the structure. Film thicknesses were about 320 nm after this treatment. Before testing the thermal stability in air and the UV stability, samples were further treated at for 2 h at 260 °C under N_2.

Preparation of BAESSQ Resin. β-Acetoxyethylsilsesquioxane (BAESSQ) resin[24,25] was prepared by the hydrolysis of (BAE)Si(OMe)$_3$ (1.15 g, 4.6 mmol) in a mixture of H_2O (1.08 g 60 mmol), THF (2.5 mL), and a catalytic amount of glacial acetic acid (60 mg). The solution was refluxed at 60−70 °C for 15 h. The volatiles were removed in vacuo to yield a clear colorless product (0.62 g, 4.462 mmol, 97% yield) as thick oil. The resin was stored in the refrigerator.

Hybrid Films Based on Staged Hydrolysis of BAESSQ. A 100-mg aliquot of BAESSQ resin was dissolved in 400 mg of diglyme and stirred overnight to achieve full solubility. PMSG (5 mg) was added into 100 mg of the above BAESSQ/diglyme solution in the dark and stirred for 2.5 h before coating. Just prior to spin-casting, 5 mg of 1.0 M TBAF/THF solution was added and mixed thoroughly. This solution was then spin-cast onto Si and quartz substrates at 2000 rpm for 60 s. The thicknesses of as-cast films were about 350 nm. The films were heated first to 170 °C under H_2O-saturated N_2 for 1 h to ensure the completed fluoride-catalyzed conversion of BAE to acetoxy groups, and to promote further condensation. After additional heating at 230 °C for 3 h under N_2, film thicknesses were about 160 nm. Before testing the thermal stability in air and the UV stability, hybrid films were further processed at 320 °C under N_2 for 2 h.

Films of PMPG. A 4-mg portion of PMPG was dissolved in 180 mg of dry THF and stirred in the dark for 4 h. The solution was spin-cast at 2000 rpm for 60 s, and the resultant films were dried in vacuo to yield films ~40 nm thick.

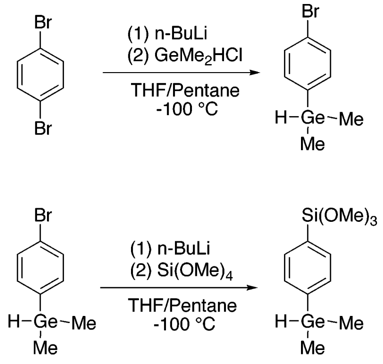
Un-Cross-Linked Films of PMSG. A 4-mg aliquot of PMSG was dissolved in 160 mg of dry THF and stirred in the dark for 3 h. The solution was spin-cast at 2000 rpm for 60 s, and the resultant films were dried in vacuo to yield films ~42 nm thick.

Cross-Linked Films of PMSG. A 4-mg portion of PMSG was dissolved in 60 mg of THF, 100 mg of ethanol, and 5 mg of 4 N HCl and stirred in the dark for 1 h. The solution was spin-cast at 2000 rpm for 60 s, and the resultant films were dried in vacuo at 120 °C, and then at 160 °C for 2 h. Film thicknesses was constant at ~92 nm before and after heating.

Results and Discussion

Monomer Synthesis. *p*-Bromophenyldimethylgermane, Br$C_6H_4GeMe_2H$, was prepared in 86% yield from the reaction of Me_2GeHCl with bromophenyllithium (generated in situ) at −100 °C (Scheme 1). Analysis by ^1H NMR indicated the product contained <1% 1,4-bis(dimethylgermyl)benzene and subsequent reactions were carried out without further purification.

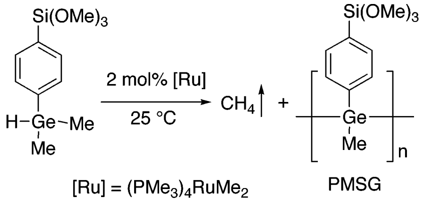
Scheme 1. Synthesis of Monomer



Lithiation of *p*-bromophenyldimethylgermane with *n*-BuLi at −100 °C followed by quenching with excess tetramethoxysilane produced dimethyl(trimethoxysilylphenyl)germane, which was isolated in 48% yield following distillation.

Polymer Synthesis. Poly(methyltrimethoxysilylphenylgermane) (PMSG) was prepared by the demethanative coupling of neat monomer using $(PMe_3)_4RuMe_2$ as the precatalyst.[18] Purification of the polymer was complicated by high solubility in methanol, the solvent typically used to precipitate polygermanes, but ~30−40% yields of purified polymer were eventually obtained by precipitation from THF/hexane at −40 °C (Scheme 2).

Scheme 2. Synthesis of Polymer by Demethanative Coupling



The ^1H NMR spectrum of PMSG in C_6D_6 revealed broad peaks between δ −0.5 and δ 1.0 (Ge−CH_3), δ 3.4−3.8 (Si−$(OCH_3)_3$), and δ 6.9−7.9 (C_6H_4). Molecular weights were determined using GPC/SEC/LS as follows: $M_n = 13\,900$, $M_w = 18\,500$, $M_w/M_n = 1.3$.

Preparation of Pure Polymer Films and Polymer−Silica Hybrid Films. Five different types of films were prepared for the examination. Thin films of pure poly(methylphenylgermane) (PMPG) and unhydrolyzed (un-cross-linked) PMSG were prepared by spin-casting polymer/THF solutions onto quartz plates, followed by drying in vacuo. Cross-linked PMSG thin films were prepared similarly by spin-casting polymer solutions to which water and catalytic HCl were added. TEOS-based hybrid films were prepared via typical sol−gel methods[26−28] using solutions of PMSG and $Si(OEt)_4$ (TEOS) with excess water and catalytic HCl. The hybrid films were then thermally cured (~160 °C) under nitrogen or vacuum. Hybrid PMSG/silica films were also prepared using the staged hydrolysis

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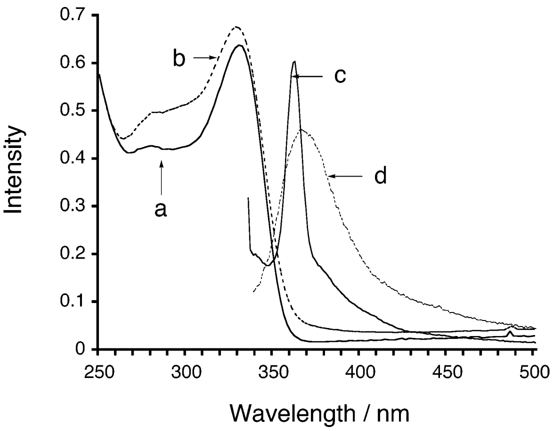
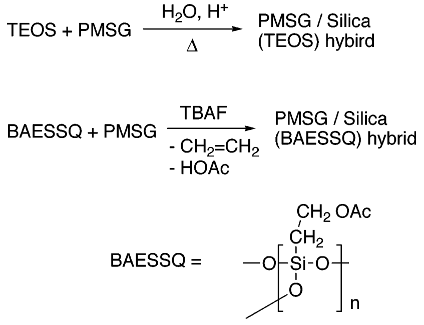


Figure 1. UV-vis absorption of PMSG in (a) THF and (b) solid film, and fluorescence emission in (c) THF and (d) solid film.

method,[24,25] by spin-casting solutions of PMSG, β-acetoxyethylsilsesquioxane (BAESSQ), and 5 mol % [Bu_4N]F (TBAF) followed by heating at 170 °C (2 h) to condense the films and at 210 °C (1 h) to remove TBAF (Scheme 3).

Scheme 3. Preparation of Organic−Inorganic Hybrid Films



UV−vis and Fluorescence Spectroscopy. The UV−vis absorption spectrum of PMSG in THF solution exhibits distinct absorbance peaks at 280 nm (aryl ring, $\pi-\pi^*$, $\epsilon = 5110$) and 330 nm (polymer backbone, delocalized GeGe $\sigma-\sigma^*$, $\epsilon = 7666$), which is very similar to the spectrum observed for poly(methylphenylgermane) ($\lambda_{\pi-\pi^*}$ ~280 nm, $\lambda_{\sigma-\sigma^*}$ ~332 nm.)[18−20] A fluorescence emission peak with $\lambda_{max} = 369$ nm (THF solution) was observed under excitation at 332 nm, again similar to that of the parent phenyl derivative.[18]

Thin films of un-cross-linked PMSG prepared by spin-casting onto quartz substrates were transparent in the visible region and exhibited absorption and emission features similar to those obtained in THF solution. Cross-linked PMSG and hybrid films prepared from PMSG with either TEOS or BAESSQ were also transparent and exhibited λ_{Ge-Ge} at ~320 nm, which is an energy about 10 nm higher than that of the polymer in THF solution. The fluorescence emission spectra of the hybrid films exhibit emission peaks with a maximum intensity at 370−380 nm that are broader than those in the films of pure PMSG. The solution and solid-state spectra of PMSG are shown in Figures 1 and 2, and summarized in Table 1.

The spin-cast films were treated with THF, and, not surprisingly, the films of PMPG and un-cross-linked PMSG dissolved completely (1 h, 25 °C), whereas cross-linked PMSG films retained 93% of absorption intensity after 1 h of treatment. The TEOS- and BAESSQ-based hybrid PMSG films showed no decrease in absorbance after 2 h in THF at 25 °C.

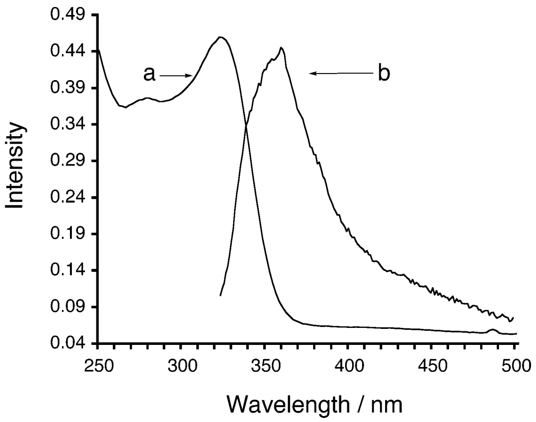


Figure 2. (a) UV−vis absorption and (b) fluorescence emission of PMSG/silica (BAESSQ) hybrid film, (~10 mol % PMSG in silica, processed at 320 °C for 2 h).

Table 1. UV-vis Absorption and Fluorescence Emission of PMSG

	UV−vis (nm)	FL emission (nm) (FWHI)
PMSG (THF)	330	369 (13 nm)
PMPG (film)	330	370 (51 nm)
PMSG (film)	332	367 (44 nm)
PMSG (cross-linked)	320	372 (79 nm)
PMSG/silica (TEOS)	318	375 (111 nm)
PMSG/silica (BAESSQ)	320	373 (91 nm)

Table 2. Weight Loss Observed by TGA

	weight loss (%)			
	≤250 °C	250−320 °C	1.5 h at 320 °C	total
silica (no PG, TEOS)	10.1	1.7	1.9	13.7
PMPG	0.6	5.3	34.0	39.9
PMPG/silica[a]	10.3	3.2	5.8	19.3
PMSG	2.9	9.3	6.8	19
PMSG/silica[b]	10.9	1.8	2.0	14.7

[a] 12 mol % (20 wt %) PMPG. [b] 11 mol % (22 wt %) PMSG.

TGA and Thermal Stability of Pure and Hybrid Polygermanes. Thermogravimetric analysis (TGA) was performed on solid powders of different samples under argon. Pure solid samples of PMPG and PMSG were examined without further treatment. Standard sol−gel derived silica was prepared by hydrolysis of a THF solution of TEOS with HCl catalyst. Hybrid materials containing PMSG or PMPG (~10 mol % v. SiO_2) were prepared by incorporating the appropriate amount of polymer predissolved in THF. All solutions were allowed to cure for 24 h at room temperature in the dark and dried for 1 h under high vacuum at room temperature. PMSG/BAESSQ hybrid materials were not included in the TGA studies, as the higher curing temperatures required in the synthesis would result in much lower initial solvent and moisture content in these samples, precluding meaningful comparisons with the other samples.

All TGA samples were heated from 27 to 320 °C at 10 °C/min and then kept at 320 °C for 90 min. For comparison, the solids derived from pure TEOS exhibited about 10.1% weight-loss below 250 °C due to loss of solvent and water, and an additional 1.7% from 250 to 320 °C (Table 2). Only 2% additional weight-loss was observed after 90 min at 320

°C (86.2% final ceramic yield.) The thermal properties of pure PMPG in argon were also examined; only 0.6% weight-loss was observed up to ca. 250 °C, with more rapid evaporation/decomposition beginning ca. 275 °C, leaving 60.1% ceramic yield (C. Y.) after 90 min at 320 °C. Similarly, a sample of pure PMSG showed ca. 3% loss up to 250 °C, then a more rapid drop in weight at higher temperatures (final C. Y. 81.0% after 90 min at 320 °C.)

The sample prepared from hydrolysis of TEOS and PMPG (∼12 mol %, 20 wt %) exhibited two main weight-loss events that mirror those in the pure samples: gradual solvent loss up to 250 °C (10.3%) as observed with the pure-TEOS-derived sample, an additional 3.2% between 250 and 320 °C, and 6.3% further loss after 90 min at 320 °C (final C. Y. 80.7%). Thus, essentially no increase or decrease in stability of PMPG is observed in the mixed material. This is not surprising, as the polygermane chains are not covalently bonded to the silica matrix in this case. In contrast, the properties of the hybrid containing PMSG (∼11 mol %, ∼22 wt %) resemble the silica derived from pure TEOS, with loss of solvent (10.9% up to 250 °C), and an additional 1.8% from 250 to 320 °C. Only minor (2.1%) further weight loss was observed after 90 min at 320 °C (final C. Y. 85.3%). Thus, no weight loss at ca. 300 °C specifically associated with polygermane decomposition was observed, consistent with a hybrid in which phenylgermane units of the polymer are covalently bonded to the silica matrix, preventing formation of volatile fragments even upon cleavage of the polygermane chain.

Effect of Thermal Treatment on Electronic Properties. Although the TGA studies showed that the hybrid materials did not degrade into volatile fragments at higher temperatures, the question of whether the conjugated Ge−Ge chains remain intact could not be determined from only the char yield. This was addressed by monitoring UV−vis absorption spectra of the thin films as a function of temperature. Films were heated at different temperatures in N_2 or in air for 1 h intervals and UV−vis absorption spectra were recorded. The spectra of pure PMPG films heated under N_2 showed no significant decrease in intensity at 325 nm after 2 h at 200 °C. However, a decrease of 21% was observed after 1 h at 230 °C. The thermal stability of pure PMPG was significantly lower in air, with a 2% decrease after 1 h at 150 °C, and 20% after 1 h at 175 °C. Not surprisingly, films of un-cross-linked PMSG behaved similarly to the parent phenyl polygermane, both in N_2 and in air. In contrast, cross-linked films of PMSG were stable for 1 h at 200 °C under nitrogen and exhibited no change in the UV−vis absorption spectrum. An 11% decrease (at 320 nm) was observed after 1 h at 230 °C, but further heating (1 h at 260 °C, 1 h at 290 °C) resulted in only 1% additional loss of absorption intensity. However, a decrease of 19% was observed after 1 h at 320 °C in nitrogen. Before testing the stability of cross-linked PMSG films in air, the samples were pretreated at 260 °C in N_2 for 2 h to ensure maximum condensation and cross-linking. However, the thermal stability of the cross-linked PMSG films in air was found to be similar to that of the PMPG and un-cross-linked PMSG films: 2% decrease in absorption intensity was found after 1 h at 150 °C, and 20% loss after 1 h at 175 °C. The results are listed in Tables 3 and 4. Thus, cross-linked films show substantially greater stability than the un-cross-linked films under N_2, but no increase in thermal stability in air.

Table 3. Loss of Ge−Ge Conjugation (%) in PMPG, PMSG, and Cross-Linked PMSG Films with Thermolysis under N_2 Measured by UV−Vis Absorption

	PMPG	PMSG	PMSG (cross-linked)
200 °C[a]	0	0	0
230 °C	21	15	11
260 °C	40	30	0
290 °C	N/A[b]	N/A	1
320 °C	N/A	N/A	19

[a] Samples heated 1 h at each temperature. [b] N/A: Extensive decomposition observed below 290 °C.

Table 4. Loss of Ge−Ge Conjugation (%) in PMPG, PMSG, and Cross-linked PMSG Films with Thermolysis under Air Measured by UV−Vis Absorption

	PMPG	PMSG	PMSG (cross-linked)
130 °C	0	0	0
150 °C	2	2	2
175 °C	20	18	20

The PMSG/Silica (TEOS) hybrid films were only slightly more thermally stable than the pure, cross-linked PMSG films, as illustrated in Figure 3 and summarized in Tables 5 and 6. One difference is that there was no loss of absorption intensity (320 nm) in the TEOS hybrid films up to 260 °C (v. 11% for the pure film), but decomposition at higher temperatures was only slightly diminished (2% after 1 h at 290 °C and 15% after 1 h at 320 °C). Similarly, the hybrid films were somewhat more stable to thermolysis in air, exhibiting a decrease of 8% in λ_{Ge-Ge} after 1 h at 175 °C.

In contrast, PMSG/silica hybrid films derived from BAESSQ maintained the σ-conjugated Ge−Ge chains at

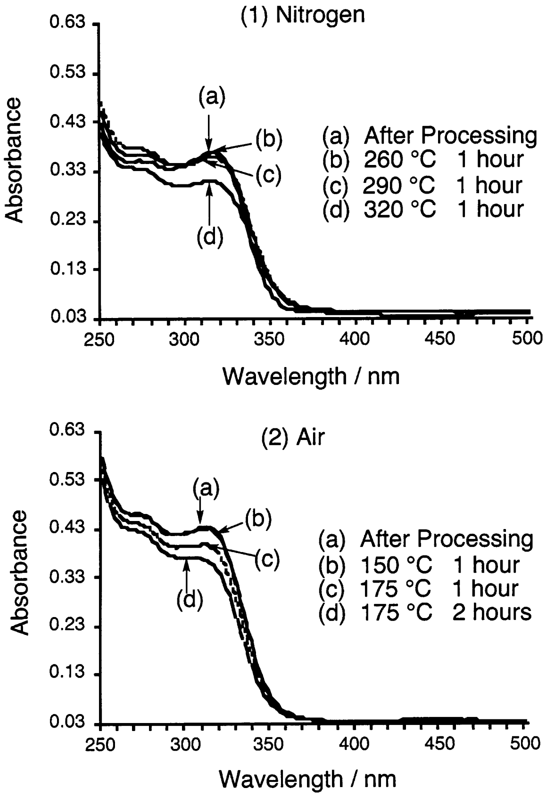


Figure 3. Thermal stability of TEOS-based hybrid films (1) under nitrogen and (2) under air.

Table 5. Loss of Ge−Ge (%) Conjugation in Hybrid Films with Thermolysis under N_2[a]

	PMSG/silica (TEOS)	PMSG/silica (BAESSQ)
260 °C	0	0
290 °C	2	0
320 °C	15	0
350 °C	N/A[b]	0
380 °C	N/A[b]	2
380 °C (16 h)	N/A[b]	10

[a] Samples heated 1 h at each temperature. [b] N/A: Extensive decomposition observed below 350 °C.

Table 6. Loss of Ge−Ge Conjugation (%) in Hybrid Films with Thermolysis under Air[a]

	PMSG/silica (TEOS)	PMSG/silica (BAESSQ)
150 °C	0	0
175 °C	8	0
200 °C	N/A	1
200 °C (12 h)	N/A	28

[a] Samples heated 1 h at each temperature.

much higher temperatures. No significant decrease of $\lambda_{\mathrm{Ge-Ge}}$ (320 nm) was observed after 2 h at 350 °C in N_2 and only ~4% decrease in $\lambda_{\mathrm{Ge-Ge}}$ was observed after 4 h at 380 °C. Remarkably, only 10% intensity loss was observed after 16 h at 380 °C under nitrogen. Although the PMSG/silica (BAESSQ) hybrid films do degrade faster in air than nitrogen, stability is significantly improved over that of the TEOS-derived hybrids. No intensity decrease at $\lambda_{\mathrm{Ge-Ge}}$ was observed after 1 h at 175 °C in air, and the films exhibited moderate stability at 200 °C in air (5% decrease in 3 h, 28% after 12 h.) In comparison, the TEOS-derived hybrid films suffered 8% loss of intensity after only 1 h at 175 °C (Figure 4).

TEOS-based hybrid films showed stability similar to that of cross-linked films in N_2, but slightly increased stability in air. These results suggest the polygermane backbone was immobilized by the cross-linking with silica matrix, and that O_2 diffusion into the films is somewhat slower. It is likely that cross-linking immobilizes the polygermane chains and in the absence of oxygen there is a decreased tendency to decompose into smaller ring or chain segments via chain "back-biting". However, cross-linking does little to prevent reaction of the σ-conjugated Ge−Ge chains with oxygen.

We have previously shown that silica matrixes generated from the staged hydrolysis of BAESSQ are significantly denser than materials formed by TEOS hydrolysis at the same temperatures. Thus, the polygermane chains should be less mobile in the BAESSQ-derived matrix, and thermal degradation due to radical diffusion and chain back-biting should be greatly reduced. In addition, the denser silica matrix would also reduce oxygen diffusion into the films, slowing oxidation of the polygermane.

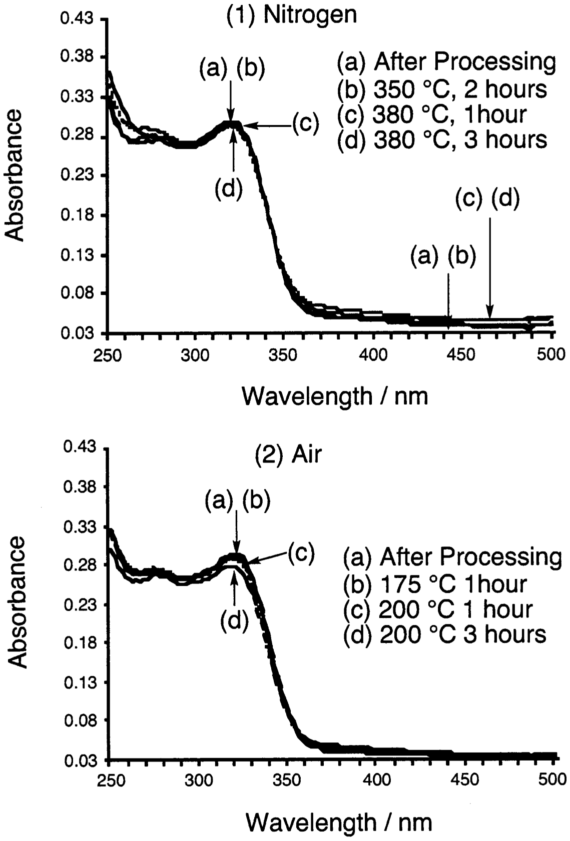


Figure 4. Thermal stability of BAESSQ-based hybrid films (1) under nitrogen and (2) under air.

Table 7. Loss of Ge−Ge Conjugation with UV Irradiation under N_2 and Air[a]

	N_2		air	
loss of $\lambda_{\mathrm{Ge-Ge}}$ intensity (%)	1 min	2 min	1 min	2 min
PMPG	30	48	50	>99
PMSG	35	75	90	>99
PMSG (cross-linked)	30	60	83	89
PMSG/silica (TEOS)	24	59	63	83
PMSG/silica (BAESSQ)	17	32	40	74

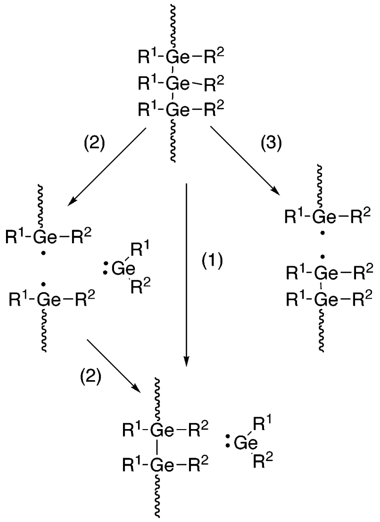
[a] 254-nm Hg UV-light, 16 mw/cm^2.

Stability to UV Irradiation. The stability of the hybrid polygermane films toward photochemical degradation was also examined. Films of cross-linked PMSG and PMSG/silica (TEOS) hybrids were first treated at 260 °C for 2 h under nitrogen before photolysis was performed using 254-nm mercury UV-light at room temperature. Hybrid films prepared from PMSG/BAESSQ were further treated at 320 °C for 2 h prior to photolysis. The stability of pure PMPG, PMSG, cross-linked PMSG, TEOS-, and BAESSQ-based hybrid films is summarized in Table 7. Note that the irradiation wavelength—254 nm—is much higher energy than the delocalized σ−σ* band responsible for the interesting electronic properties of polygermanes.

Not surprisingly, all samples were more stable to UV photolysis under nitrogen than in air. In N_2, cross-linked PMSG films and the TEOS-based hybrid films exhibited similar stability, but better stability than un-cross-linked films of pure PMPG and PMSG. Once again, the BAESSQ-based hybrid films exhibited the greatest stability.

Photolysis of polysilanes and polygermanes has been investigated by several groups. Three concurrent and competing reactions are likely (Scheme 4).[9−12] Process (1) involves the concerted extrusion of germylene and shortening of the Ge_x chain. Process (2) is similar, but stepwise, and would generate the germylene and two intermediate germyl radicals which could subsequently rapidly recombine. Michl has suggested that this stepwise path is energetically inaccessible for polysilanes with irradiation at 254 nm,[10] although the analogous process would require less energy for polyger-

Scheme 4. Mechanism of the Photodegradation of Polysilanes



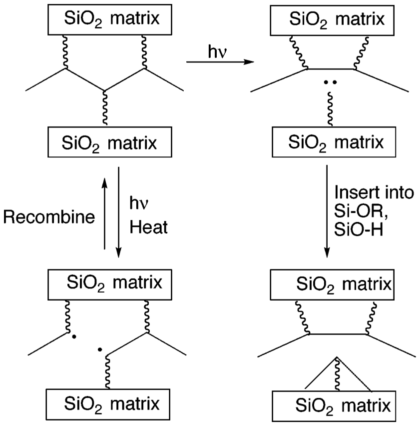
manes. Process (3) is the simple homolytic cleavage of the polymer chain into radical terminated segments, which can either recombine or be scavenged, similar to the thermal degradation route.

One would expect the photogenerated radicals to behave similarly to those generated thermally, thus the stability increases associated with chain immobilization in the hybrid films should also apply. However, extrusion of germylene is unique to the photochemical process, and germylene reactivity is quite distinct from that of germyl radicals. It is well-known that silylenes insert readily into Si−OR and O−H bonds,[29−32] whereas the reaction of silyl radicals with these strong bonds are slow and often thermodynamically unfavorable. The chemical behavior of germylenes is similar to that of silylenes,[33−35] and insertion into O−H and R−OH bonds has been observed. Although germylene insertion into Si−OR bonds has not been reported, it is likely this would be thermodynamically accessible.

In other words, immobile germyl radicals produced either thermally or photochemically in the silica matrix of the hybrid material have little alternative to recombination (in the absence of oxygen). On the other hand, photochemically generated germylenes can potentially react irreversibly with the Si−O−Si and residual SiO−H and Si−OR groups that form the encapsulating matrix. Unlike in the case of germyl radicals, covalently anchoring the germylene to the matrix does not preclude undesirable reactions.

As in the thermal studies, the greater photochemical stability of the BAESSQ/PMSG hybrids is likely attributable to a greater degree of condensation and densification, which both decreases fragment mobility and lowers the concentration of residual SiOH and SiOR groups that could react with the germylene intermediates (Scheme 5).

Scheme 5. Proposed Reactions in Hybrid Films



Conclusions

Covalent binding of arylmethylpolygermanes into hybrid silica materials leads to substantial increases in thermal stability without degrading Ge−Ge σ-conjugation as measured by UV−vis absorption and fluorescent emission spectroscopy. For example, only 2% decrease in $\sigma-\sigma^*$ intensity is observed after 1 h at 380 °C under nitrogen, compared with 21% decrease at 230 °C for the parent poly(methylphenylgermane) (PMPG). In general, silica hybrids formed by condensing poly(methyltrimethoxysilylphenylgermane) with BAESSQ exhibited much greater stability enhancements than those prepared by traditional sol−gel methods using TEOS. In both cases, the thermal stability of the hybrids under air was substantially lower than that under nitrogen, but was still improved over that of the pure polygermanes. The gains in stability toward photolysis (254 nm) are significant, but much less dramatic than in the case of thermal exposure. These results are consistent with the idea that covalently anchoring each germanium in the polymer chain to the silica matrix reduces mobility of germyl radicals produced by both thermolysis and photolysis, leading to efficient recombination to restore the Ge−Ge chains under nitrogen. Permeation of oxygen into the hybrid materials during thermolysis in air, however, leads to irreversible trapping of the germyl radicals. On the other hand, germylene intermediates—generated only during photolysis—are more reactive and can combine irreversibly with Si−O−Si bonds or residual SiOH groups in the silica matrix, thus leading to faster photolytic degradation of the conjugated Ge−Ge chains, even under nitrogen.

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