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## DEACTIVATION OF FUSED-SILICA CAPILLARY COLUMNS WITH POLYMETHYLHYDROSILOXANES

### OPTIMIZATION OF REACTION CONDITIONS

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#### SUMMARY

An evaluation of reaction conditions for surface deactivation of fused-silica capillary columns with polymethylhydrosiloxanes (PMHS) is given. Deactivation was accomplished by a dehydrocondensation reaction between the silylhydride bonds of PMHS and the surface silanols of fused silica. This provided a bonded, low surface tension film wettable by polydimethylsiloxane stationary phases. The percentage of silylhydride groups in the polymer influenced the required reaction time at 300°C. Hydrolysis of Si–H bonds by physically adsorbed water played a role in providing complete surface coverage of the deactivation layer. The exclusion of oxygen was imperative during the dehydrocondensation reaction. Reaction temperatures for thermally initiated dehydrocondensation of silanol and silylhydride, silylhydride oxidation, and silylhydride hydrolysis were determined.

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#### INTRODUCTION

Non-polar (methyl) surface deactivation of capillary columns has been the topic of numerous published works in the past decade. Three of the most frequently used methods for glass and fused-silica columns are high temperature silylation<sup>1</sup>, polysiloxane degradation<sup>2</sup>, and cyclic siloxane deactivation<sup>3</sup>. The critical surface tension achieved with these methods<sup>4</sup> is 21 mN m<sup>-1</sup>. These surfaces are wetted by polydimethylsiloxane stationary phases. However, these methods require such high reaction temperatures (400–450°C) that oxidation of the protective polyimide coating on the capillary decreases its flexibility and transparency. A recently reported deactivation method alleviates this problem by using a reactive polymethylhydrosiloxane (PMHS) fluid to block surface silanol groups at 250–300°C<sup>5</sup>.

Heat treatment of an applied thin coating of PMHS has been found to provide a surface-bonded film with low critical surface tension (20 mN m<sup>-1</sup>)<sup>6</sup>. In addition, physically adsorbed water hydrolyzes Si–H bonds to Si–OH groups which further dehydrocondense with Si–H bonds or condense with other Si–OH groups to form a highly crosslinked resin film<sup>7</sup>.

Fused-silica capillary columns have been deactivated with PMHS fluids at 250°C<sup>5</sup>, the deactivating reaction being the dehydrocondensation of silanol groups on the fused-silica surface with reactive Si-H bonds of the PMHS polymer, establishing surface-to-polymer bonding. The only by-product of the reaction is hydrogen gas.

The factors affecting the optimization of the PMHS deactivation method are discussed in this paper. Reaction temperatures of non-catalyzed dehydrocondensation between silylhydride and surface silanols, and oxidation and hydrolysis of Si-H bonds were experimentally determined. Effects of polymer Si-H percentage on the required reaction time at 300°C, and the effect of increased reaction pressure, caused by hydrogen gas formation, on the degree of deactivation were studied. The contribution of, and the sequence in which silylhydride hydrolysis, silanol-silanol condensation, and silylhydride-silanol dehydrocondensation occur during deactivation of fused-silica capillaries were established.

## EXPERIMENTAL

### *Materials*

PMHS (50% Si-H, 85 cs fluid), polydimethyl-(50-55%)methylhydro(45-50%)siloxane co-polymer (PDM-MHS, 25% Si-H, 10-15 cs fluid), polydimethyl(82-85%)methylhydro(15-18%)siloxane co-polymer (PDM-MHS, 9% Si-H, 25-35 cs fluid) and 1,1,3,3-tetramethyl-1,3-dihydrodisiloxane (TMDS) were obtained from Petrarch Systems (Bristol, PA, U.S.A.). Triphenylsilanol (TPS) was obtained from Silar Laboratories (Scotia, NY, U.S.A.). Capillary gas chromatography-mass spectrometry (GC-MS) (Hewlett-Packard 5982A, described later) analysis of PMHS (50% Si-H) revealed it to be a mixture of linear and cyclic oligomers. The Si-H percentages of the three polymers were calculated from <sup>1</sup>H NMR analysis to be 48 ± 1% for PMHS, 20 ± 1% for PDM-MHS (25% Si-H), and 6 ± 1% for PDM-MHS (9% Si-H). TMDS was found to contain 32.4 ± 0.2% Si-H by Fourier transform (FT)-NMR (JEOL FX90Q). TPS was determined by capillary GC-MS to be greater than 99.9% pure. These organosilicon compounds were used as obtained from the supplier without further purification. Fused-silica capillary tubing of 320 μm I.D. (Hewlett-Packard, Avondale, PA, U.S.A.) was used in this study.

### *Preparation and testing of capillary columns*

Six 10-m columns were deactivated with the three polymers (9%, 25% and 50% Si-H, two columns each) in the manner outlined previously<sup>5</sup>. However, these columns were sealed immediately after the solvent rinsing step and were not coated with stationary phases. These columns were connected, via a zero dead-volume butt connector, to the end of a PMHS-deactivated 15 m × 320 μm I.D. column coated with a 0.25-μm film of SE-54 (Applied Science, State College, PA, U.S.A.). The connected columns were placed in a Carlo Erba 4160 Fractovap gas chromatograph equipped for split injection and flame ionization detection (FID) for evaluation. Hydrogen carrier gas linear velocities were maintained at 30-40 cm s<sup>-1</sup> with split ratios of 50-100:1.

The solute test mixtures used to evaluate the capillary surface neutrality and

inertness were reported earlier<sup>5</sup>. All chromatograms were obtained based on a 2–5 ng full-scale response for alkanes ( $1 \cdot 10^{-11}$  A f.s.). Basic and acidic test mixtures were injected at 40°C, and after a 2-min isothermal period, the oven was programmed at 4°C min<sup>-1</sup> up to 160°C.

#### *Oxidation, hydrolysis, and dehydrocondensation of Si-H*

*Reactions with TMDS.* Oxidation of TMDS was carried out with TMDS (150 mg) sealed in dehydrated (280°C for 24 h) test tubes with 6 cm<sup>3</sup> of air. Four samples were heated from 40°C at 8°C min<sup>-1</sup> to 50°C, 100°C, 150°C, or 250°C, respectively, and held at the upper temperature for 3 h. For an additional four samples, the final temperature of 250°C was held for 0.5, 1, 6, and 18 h, respectively. An additional sample was heated to 250°C for 10.5 h.

Hydrolysis of TMDS was carried out by reacting TMDS (250 mg) and distilled-deionized water (30 mg) in test tubes sealed under argon gas. Strict precautions were taken in working with samples containing TMDS and water, since high hydrogen gas pressures were obtained. Blanks were run by heating TMDS, under an argon atmosphere, to the temperatures and times outlined under oxidation above.

The dehydrocondensation reaction was studied by mixing TMDS (240 mg) and TPS (50 mg) in each of eight dehydrated glass test tubes. These samples were carefully sealed under argon gas and heated for the same times and temperatures outlined for the oxidation reaction.

*Reactions with PMHS.* Oxidation of PMHS was carried out by sealing PMHS (40 mg) with 6 cm<sup>3</sup> of air in dehydrated glass test tubes as previously described. These were heated at 100°C, 180°C, or 250°C for 14.5 h.

Hydrolysis of PMHS was studied by heating argon purged and sealed tubes containing PMHS (40 mg) and distilled-deionized water (30 mg) to 100°C, 180°C, or 250°C for 14.5 h. Strict safety precautions were again taken upon opening these containers.

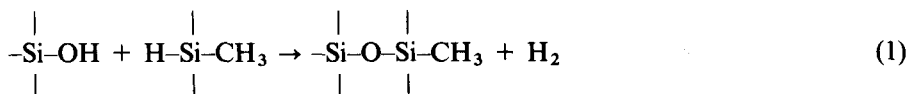
The dehydrocondensation reaction was studied by heating 1:1 mixtures of PMHS (85 cs fluid) and TPS. These mixtures were sealed under argon gas within dehydrated glass test tubes. Each mixture was heated from 40°C at 8°C min<sup>-1</sup> to 100°C, 180°C, or 250°C, respectively, and held for 14.5 h.

*Analysis of reaction products.* A homogeneous sampling (10–20 mg) of the described TMDS reaction products were dissolved in deuterated chloroform for <sup>1</sup>H NMR analysis. The dichloromethane-soluble fraction of the reaction products from selected samples were coated on sodium chloride plates and analyzed by FT-IR spectroscopy.

Dehydrocondensation reaction products of TPS and PMHS, as well as TPS and TMDS, were analyzed by capillary column GC-MS. The samples were injected using a cold on-column injector. A 23 m × 320 μm I.D. PMHS-deactivated SE-54 (0.25 μm film thickness, *d<sub>f</sub>*) coated column was temperature programmed in an HP 5710A gas chromatographic oven at 8°C min<sup>-1</sup> from 40°C to 300°C. A Hewlett-Packard 5982A GC-MS system (70 eV ionization voltage) was scanned from 50–600 a.m.u. every 3 s.

## RESULTS AND DISCUSSION

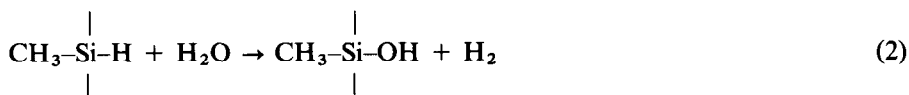
The reaction chiefly responsible for covalent bonding between surface silanols and PMHS is represented in eqn. 1<sup>8</sup>.



This is known as a dehydrocondensation reaction. Hydrogen gas is the by-product of this siloxane forming reaction<sup>9</sup>. Dehydrocondensation occurs more readily under capillary column acidic conditions (hydride ion formation from Si-H is the favored initial step) than under conditions of higher pH, in which deprotonation of Si-OH is favored.

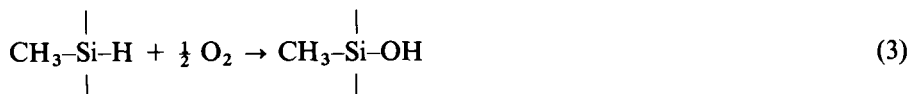
The methyl group is slightly electron donating to silicon. Methyl substitution increases reactivity of the Si-H bond relative to electron withdrawing groups<sup>6,10</sup>. The Si-H bonds of PMHS are, therefore, sufficiently reactive to dehydrocondense with surface silanols without acid catalysts. When deactivating with PMHS, one should first remove hydrochloric acid and nitric acid impurities present in the capillary in order to maintain control of the pH and stability of the deactivation film.

Hydrolysis of the Si-H bond (eqn. 2) is responsible for perpetrating most of the intra- and intermolecular crosslinking of PMHS<sup>7</sup>.



The hydrogen-bonded layer of water on fused silica induces initial hydrolysis at the PMHS-water interface. This is followed by condensation of the intermediate silanols to create tertiary functionality in the polysiloxane deactivation film<sup>11</sup>. At room temperature, Si-H hydrolysis occurs most readily under basic conditions, slightly slower in highly acidic environments (as found in fused-silica capillary tubing), and slowest in solutions between pH 5-7<sup>12</sup>. The rate of Si-H hydrolysis under capillary column acidic conditions and at 300°C is quite spontaneous and irreversible.

Silylhydride bonds can also be oxidized to silanol groups by atmospheric oxygen, as given in eqn. 3<sup>13</sup>.



In contact with oxygen, Si-H bonds sluggishly oxidize (eqn. 3) to form silanols at elevated temperature or in the presence of specific catalysts. Silylhydride oxidation has been observed at as low as 80-180°C, depending upon catalytic conditions<sup>13</sup>. However, the role of Si-H oxidation in crosslinking of PMHS<sup>14</sup> has been established as minute in comparison with the effect that trace moisture-induced Si-H hydrolysis has on PMHS crosslinking<sup>8</sup>.

The required reaction time at 300°C for complete deactivation of fused-silica capillaries was determined for polysiloxanes containing 9–50% molar Si–H bonds. After being heated to 300°C for only 0.5 h, PMHS (50% Si–H) provided the most neutral and inert surface. The degree of surface neutrality decreased with decreasing Si–H content. However, all fused-silica capillaries deactivated with the same three reagents at 300°C for 4 h were neutral, inert, and nearly indistinguishable.

Eqn. 1 shows that the positive hydrogen pressure that is built up during the deactivation heat treatment could affect the rate of dehydrocondensation. However, capillaries sealed with dry nitrogen or argon gas at near atmospheric pressure provided surface inertness and neutrality equal to columns deactivated under vacuum. Interestingly, the volume of hydrogen gas evolved was observed to be proportional to the capillary surface water content. In all cases, the hydrogen gas build-up did not affect the degree of surface neutrality achieved.

The dimer, TMDS, was substituted for PMHS in several studies of reactions involving Si–H bonds. PMHS polymers were found to crosslink into insoluble resins upon hydrolysis or oxidation, making them difficult to chromatographically or spectroscopically analyze. However, the hydrolysis and oxidation reaction products of TMDS were soluble in [<sup>2</sup>H]chloroform for <sup>1</sup>H NMR analysis and were volatile enough for capillary GC separation. In the <sup>1</sup>H NMR spectra of Fig. 1, the position

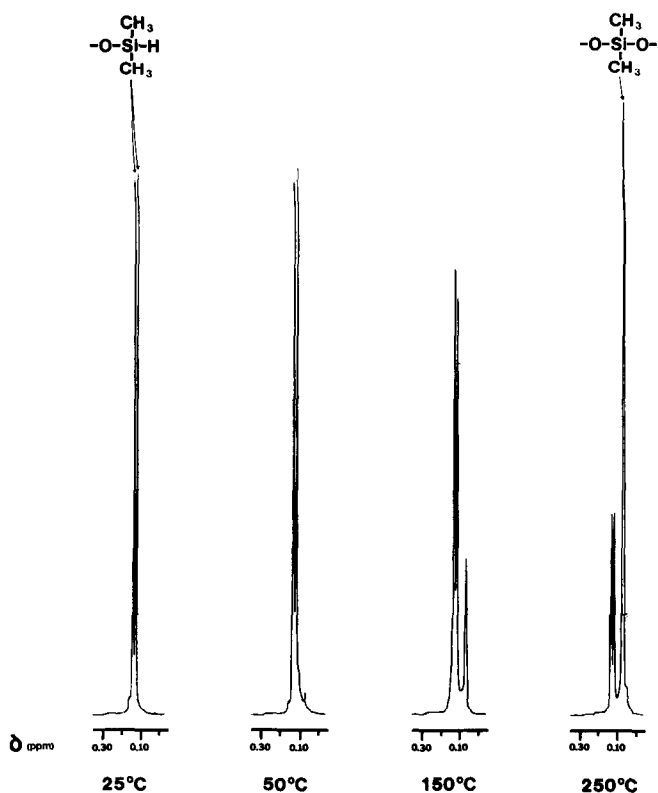


Fig. 1. <sup>1</sup>H FT-NMR spectra of the hydrolysis products of TMDS after heating to 25°C, 50°C, 150°C, and 250°C for 3 h.

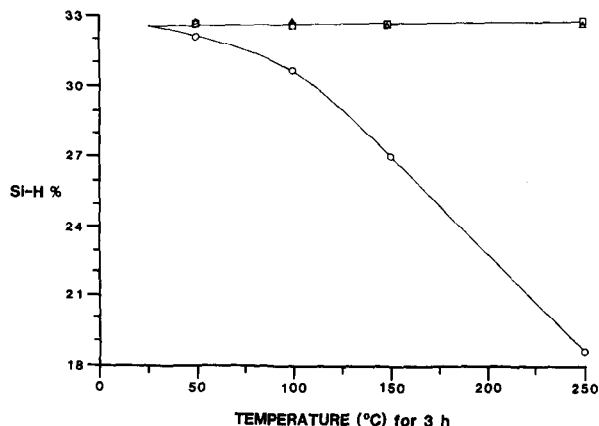


Fig. 2. TMDS percent Si-H vs. temperature (for 3 h). Data obtained from  $^1\text{H}$  FT-NMR spectra of ( $\Delta$ ) TMDS and argon gas, ( $\square$ ) TMDS and air, and ( $\circ$ ) TMDS and water and argon gas.

of the symmetrical doublet ( $\delta = 0.185$  and  $\delta = 0.155$  ppm; [ $^2\text{H}$ ]chloroform reference) corresponding to the methyl hydrogens of the  $-\text{O}_{1/2}-\text{Si}(\text{CH}_3)_2\text{H}$  segments of TMDS was shifted downfield from the singlet ( $\delta = 0.052$  ppm) of the methyl hydrogens of the  $-\text{O}_{1/2}-\text{Si}(\text{CH}_3)_2-\text{O}_{1/2}-$  segments of linear  $\alpha,\omega$ -bis(dimethylhydrosiloxy)polydimethylsiloxanes produced during temperature induced hydrolysis or oxidation. Using TMDS in place of PMHS made it easier to determine the extent and rate of Si-H reactions with Si-OH, water, and oxygen. Heated to  $300^\circ\text{C}$  in an anhydrous atmosphere of nitrogen, argon, helium, or vacuum, organosilicon hydrides remain unaltered. PMHS showed no signs of polymerization or crosslinking under the same conditions. This was confirmed by  $^1\text{H}$  NMR, in that the dimer, TMDS, showed no substantial loss in Si-H percentage when heated in the absence of oxygen and water, as depicted in Figs. 2 and 3.

The non-catalyzed, thermally initiated dehydrocondensation reaction was

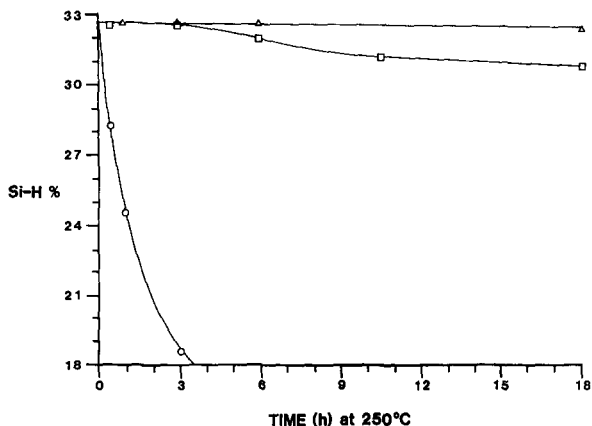


Fig. 3. TMDS percent Si-H vs. time (at  $250^\circ\text{C}$ ). Data obtained from  $^1\text{H}$  FT-NMR spectra of ( $\Delta$ ) TMDS and argon gas, ( $\square$ ) TMDS and air, and ( $\circ$ ) TMDS and water and argon gas.

studied first. From the chromatograms in Fig. 4, it can be seen that dehydrocondensation between Si-H bonds and Si-OH groups was slightly apparent at 150°C. Glass reaction tubes containing TMDS and TPS, and heated to 150°C and 250°C showed

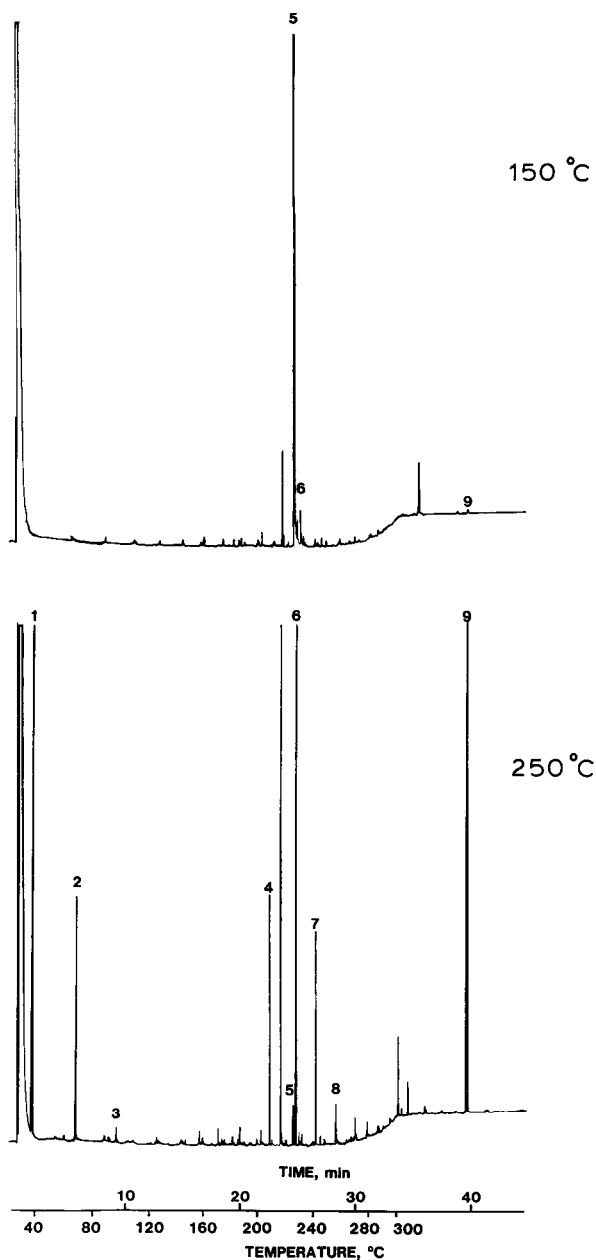


Fig. 4. Gas chromatograms of the reaction products of TMDS and TPS formed at 150°C and 250°C for 3 h. Conditions: hydrogen carrier gas ( $50 \text{ cm s}^{-1}$ ), temperature programmed at  $4^\circ\text{C min}^{-1}$ , split injection, and FID ( $1 \times 10^{-11} \text{ A f.s.}$ ). Labeled peaks identified in Table I.

evidence of hydrogen build-up after reaction (eqn. 1). However, no pressure release was observed and no dehydrocondensation products of TMDS and TPS were found at or below 100°C. Additionally, from Fig. 4, one can see that at 150°C, only small

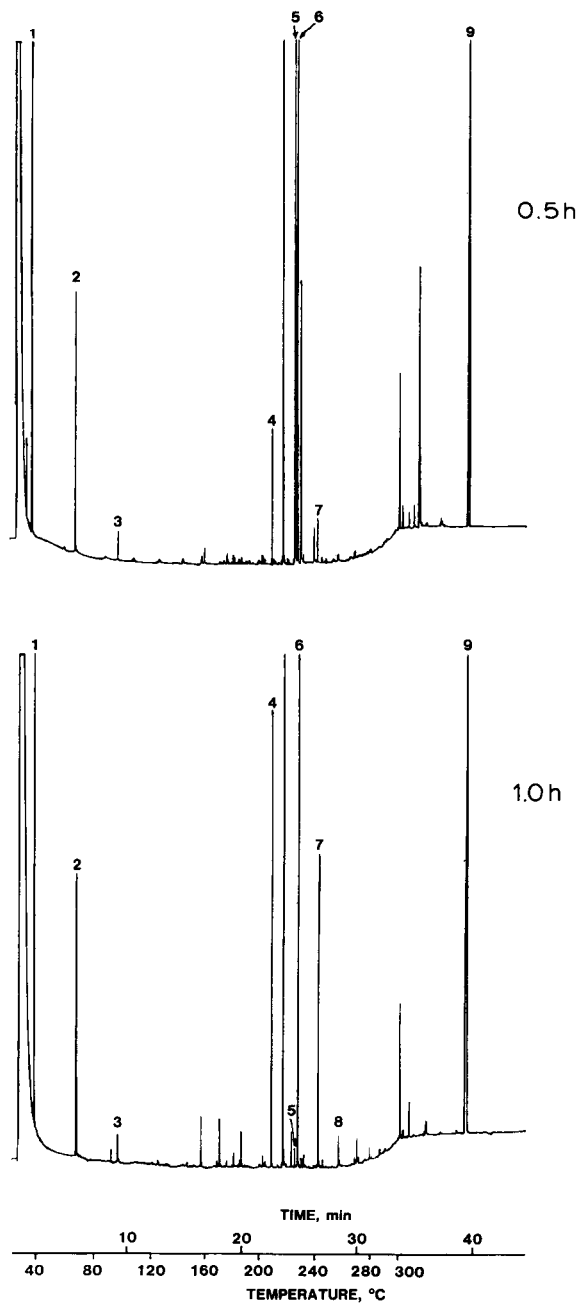


Fig. 5. Gas chromatograms of the reaction products of TMDS and TPS formed at 250°C for 0.5 and 1.0 h. Conditions same as in Fig. 4. Labeled peaks identified in Table I.



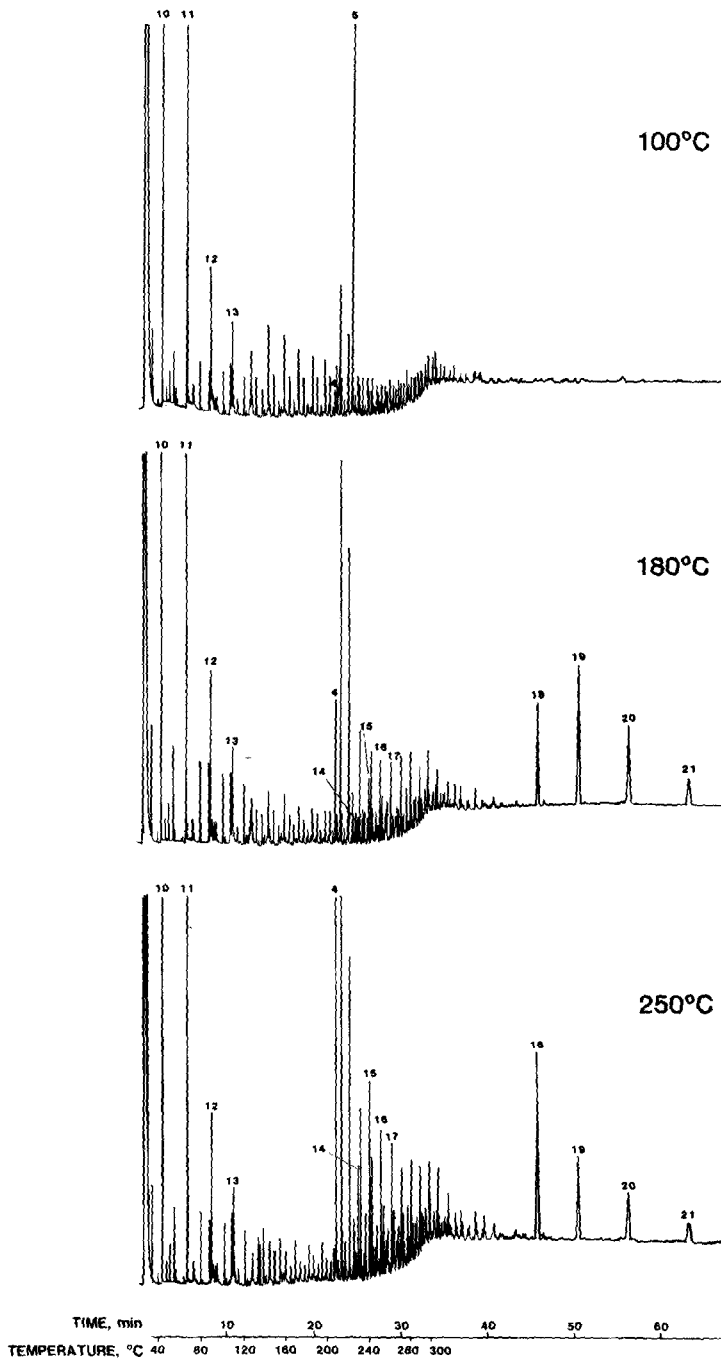


Fig. 6. Gas chromatograms of the reaction products of PMHS and TPS at 100°C, 180°C, and 250°C for 14.5 h. Conditions: same as in Fig. 4. Labeled peaks identified in Table I.



amounts of TPS had dehydrocondensed with TMDS, whereas at 250°C (when all TPS was consumed), 25% of the TPS reaction products were dehydrocondensation products (peaks 6–8). From Fig. 5, one can see that dehydrocondensation of TPS and TMDS was partially completed after just 0.5 h at 250°C, and totally completed after 1 h. One reason that the dehydrocondensation reaction proceeds swiftly to completion is because it is irreversible. Incidentally, after heating TMDS and TPS at 250°C for 3 h, no silanol functionality was detected by FT-IR spectroscopy, and no TPS was found by capillary GC-MS of the reaction products. The chromatogram in Fig. 4 (lower) shows that the largest fraction of TPS (30–40%) had condensed to form hexaphenyldisiloxane (peak 9). In the same chromatogram, it can also be seen that dehydrocondensation of TPS and TMDS [as well as other  $\alpha,\omega$ -bis(dimethylhydrosiloxy)polydimethylsiloxanes] was quite apparent. These dehydrocondensation products were tentatively identified by capillary GC-MS to be linear  $(C_6H_5)_3Si[-O-Si(CH_3)_2]_n-O-Si(CH_3)_2H$  (20% of original TPS) with  $n = 1-3$  (peaks 6–8, see Table I). Interestingly, 2–5% of the original TPS was also reduced by Si-H bonds to triphenylhydrosilane (peak 4)<sup>15</sup>. The other peaks were tentatively identified as silanolysis products (condensation through cleavage of Si-C bonds by Si-OH) or products from coupling reactions involving the displacement of Si-H hydrogens by phenyl groups.

The dehydrocondensation of PMHS and TPS at various temperatures and at 250°C for various lengths of time produced results similar to the TMDS and TPS experiments. The chromatograms in Fig. 6 show the reaction products of PMHS and TPS obtained at three different temperatures. Even at as low as 100°C, TPS was reduced to triphenylhydrosilane (peak 4) by PMHS. At 180°C, mono- (peaks 14–17) and disubstituted (peaks 18–21) triphenylsiloxy TMDS dehydrocondensation products appeared. The chromatogram of the PMHS and TPS 250°C reaction products shows a higher concentration in the mono- *versus* the disubstituted TPS dehydrocondensation products. Interestingly, no TPS condensation product (hexaphenyldisiloxane) was formed in the presence of PMHS, as was formed when TPS was reacted with TMDS (Figs. 4 and 5). This is best explained by the fact that above 150°C, the greater Si-H:Si-OH ratio of the PMHS and TPS combination favored silylhydride-silanol dehydrocondensation over silanol-silanol condensation.

From the combined TMDS and PMHS data, the non-catalyzed, thermally initiated reaction temperature of eqn. 1 was determined. It was assumed that the silanol of TPS and fused-silica surface silanols show similar reactivity with TMDS and PMHS<sup>16</sup>. Using this assumption, dehydrocondensation of fused-silica surface silanols with Si-H bonds occurs only slightly at 150°C, moderately at 180°C, and actively at and above 250°C (Figs. 4–6).

In addition to the dehydrocondensation reaction, water and oxygen also react with Si-H bonds to increase the total number of silanol groups and, hence, lead to intra- and interpolymeric chain condensation. The effects that water and oxygen have on the final deactivated surface cannot be ignored, and therefore, the temperatures of the thermally initiated, non-catalyzed hydrolysis and oxidation reactions of Si-H bonds of TMDS and PMHS were determined.

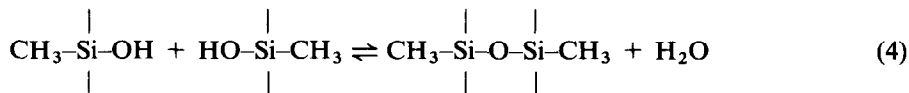
Silylhydride oxidation is a method of forming silanol groups<sup>13</sup>. However, FTIR analysis of TMDS and PMHS samples heated in the presence of oxygen showed that no silanol functionality existed in the final products. Upon oxidation,

TMDS polymerized into a narrow distribution of linear  $\alpha,\omega$ -bis-(dimethylhydro-siloxy)polydimethylsiloxanes with up to 6 dimethylsiloxy units, while PMHS cross-linked into a dichloromethane insoluble resin. Oxidation of the Si-H bonds of TMDS and subsequent condensation or dehydrocondensation were only measureable after periods of 6 h and longer at 250°C (Fig. 3), the products being linear  $\text{H}(\text{CH}_3)_2\text{Si}(-\text{O}-\text{Si}(\text{CH}_3)_2)_n-\text{O}-\text{Si}(\text{CH}_3)_2\text{H}$  (with  $n = 0-6$ ) and hydrogen gas. Such oxygen induced polymerization, as discussed by Noll<sup>13</sup>, likely occurs via dehydrocondensation of silylhydrides and intermediate silanols (formed via Si-H oxidation) above 150°C to produce siloxane bonds and hydrogen gas. In addition to oxidation of Si-H bonds, it has also been shown that oxygen oxidizes methyl groups attached to the siloxane backbone at an appreciable rate, even at as low as 200–250°C<sup>17-19</sup>. Such oxidation induces homolytic scission of Si-C bonds and produces methanol, formaldehyde, and formic acid from the methyl radicals and hydroxyl groups on the silicon radicals<sup>19</sup>. These newly formed silanols have been shown to condense, thereby crosslinking polydimethylsiloxanes into insoluble gels<sup>20</sup>. The aforementioned oxidized single carbon compounds accelerate depolymerization<sup>18</sup>, act as active hydrogen bonding moieties, and thermally decompose to water, carbon dioxide, carbon monoxide, and hydrogen gases<sup>17,19</sup>. Heat treatments of PMHS coated fused-silica capillaries contaminated with oxygen produced active surfaces causing frequent incidence of ghost peaks. Thus, the detrimental effect of oxygen in the PMHS deactivation of fused-silica capillaries is likely attributed to the oxidation of Si-CH<sub>3</sub> groups and not to the oxidation of Si-H bonds. Therefore, oxygen must be eliminated from the PMHS coated capillary via extensive nitrogen or argon purging in order to assure neutrality and inertness of the modified fused-silica surface.

At elevated temperatures and under acidic conditions (similar to those found in fused-silica capillaries) water readily hydrolyzes Si-H bonds to Si-OH groups<sup>12</sup>. However, spectroscopic analyses of TMDS and PMHS hydrolysis products showed that no silanol functionality existed. Reversible silanol-silanol condensation sluggishly follows Si-H hydrolysis at moderate temperatures (above 100°C), while rapid and irreversible silanol-silylhydride dehydrocondensation dominates at 200°C and above. The hydrolysis products of PMHS were insoluble foams and hard amorphous silicas caused by the abundance of hydrogen gas formed during the reaction (eqns. 1 and 2). The hydrolysis and dehydrocondensation (or condensation) products of TMDS were again linear  $\alpha,\omega$ -bis(dimethylhydro-siloxy)polydimethylsiloxanes, with the number of dimethylsiloxy units ranging from one to more than twenty. The degree of polymerization of TMDS and crosslinking of PMHS was much higher from hydrolytic than from oxidative conditions. According to the <sup>1</sup>H NMR spectra depicted in Fig. 1 and the <sup>1</sup>H NMR data plotted in Fig. 2, hydrolysis of TMDS was not detectable at room temperature, but was apparent at 50°C and quite obvious at higher temperatures. Hydrolysis of PMHS was also undetectable at room temperature, but at 100°C, 180°C, and 250°C, hard foams and silicas, still containing Si-H bonds, were produced. Enormous pressure releases caused by escaping hydrogen gas were observed upon opening the glass tubes containing the 100°C, 180°C, and 250°C hydrolysis products of PMHS. The hydrolysis of Si-H bonds of TMDS and PMHS was not appreciable at room temperature, but was quite favorable above about 50°C.

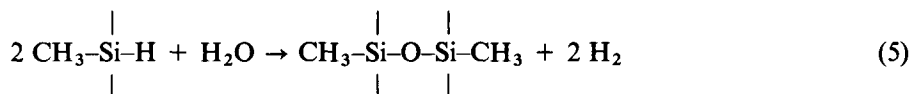
Since the hydrolysis of Si-H bonds to Si-OH groups occurs at even moderate temperatures, condensation of these silanols can occur according to two different

pathways to give siloxane bonds. The less dominant pathway is the condensation of silanols as outlined in eqn. 4:



The rates of condensation of dimethylsilanediols and silanol terminated polydimethylsiloxanes are initially very high under acid catalysis or dehydrating conditions<sup>21</sup>. More importantly, the silanol-silanol condensation reaction is reversible in the presence of water formed in the reaction. Therefore, the rate of condensation can be increased by heating the reaction mixtures above 100°C and purging them with inert gas to drive off the evolved water<sup>21</sup>. Non-catalyzed condensation of TPS in a closed system to form hexaphenyldisiloxane began to occur at 150°C (33% of TPS had condensed), while at 200°C and 250°C, 97% and 99% of TPS had condensed, respectively. Even at 250°C for 3 h, TPS was still present due to the reversibility of eqn. 4 in the presence of evolved water. Fortunately, additional Si-H bonds irreversibly take up any produced water, allowing the hydrolysis-condensation reaction to proceed more towards completion.

The second and most dominant pathway for the condensation of silanols produced from Si-H hydrolysis is the irreversible dehydrocondensation reaction (eqn. 1). We have shown that this reaction occurs irreversibly and to a significant extent at as low as 200°C. Dehydrocondensation should dominate as the silanol consuming reaction at and above about 200°C, since at any given time, the number of silanols formed is insignificant to the number of Si-H bonds present. Therefore, the dehydrocondensation pathway is kinetically favored over silanol-silanol condensation during the initial temperature programming (above 200°C) and throughout the final deactivation heating at 300°C. The overall irreversible hydrolysis-dehydrocondensation reaction consumes water and produces hydrogen gas as the only by-product, as written in eqn. 5:



In conclusion, the optimum deactivation conditions have been found to include purging the capillary with an inert gas at 250°C for about 2 h. After this moderate dehydration, the capillary is coated with PMHS, sealed under argon or nitrogen gas, and deactivated at 300°C for 4 h. The non-catalyzed, thermally initiated Si-H hydrolysis occurs rapidly at any temperature above about 50°C and dehydrocondensation of Si-H and Si-OH begins to become apparent at about 200°C. Reaction of PMHS on fused-silica surfaces is dominated by hydrolysis-dehydrocondensation of Si-H bonds by surface adsorbed water to form a crosslinked film and continues with the dehydrocondensation of remaining Si-H bonds of this resinous film with surface silanols to bond the crosslinked film to the substrate, making the surface inert and neutral. Processes occurring during capillary surface modification and deactivation with PMHS are a combination of reactions involving reactive Si-H bonds.

## ACKNOWLEDGEMENT

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