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DEACTIVATION OF FUSED-SILICA CAPILLARY COLUMNS WITH POLYMETHYLHYDROSILOXANES

CHARACTERIZATION OF THE DEACTIVATED SURFACE

C. L. WOOLLEY, K. E. MARKIDES* and M. L. LEE*

Department of Chemistry, Brigham Young University, Provo, UT 84602 (U.S.A.)

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SUMMARY

Characterization of polymethylhydrosiloxane (PMHS) deactivated fused-silica capillary columns is described. The PMHS modified surface was shown to be neutral and inert. The thickness of the PMHS surface modification was close to a monolayer. The deactivation film was non-extractable by organic solvents and showed high thermal stability. The critical surface tension (γ_c) of this methylsiloxane film was similar to other high temperature methyl deactivated surfaces. No unreacted silylhydride (Si-H) bonds were detected on the deactivated surface. Various experiments confirmed the bonding of the film via surface silanol-silylhydride dehydrocondensation. The physical structure of the surface film is described using evidence obtained.

INTRODUCTION

Significant improvements in surface deactivation and modification of fused-silica capillary columns have been made during the last several years. The common high temperature (400–450°C) deactivation methods, high temperature silylation^{1,2}, polysiloxane degradation^{3,4}, and cyclic siloxane deactivation^{5,6}, have proven useful in obtaining neutral and inert surfaces prior to coating polydimethylsiloxane stationary phases. A novel, lower temperature (250–300°C) method utilizes combined cyclic and linear polymethylhydrosiloxane (PMHS) oligomers to modify the column surface^{7,8}. Dehydrocondensation of surface silanols with PMHS silylhydrides (Si-H) bonds the oligomers to the substrate. The by-product of this surface modifying reaction is hydrogen gas. The low reaction temperature leaves the polyimide of fused-silica capillary columns clear and flexible.

The characterization of successfully deactivated surfaces has proven useful to the description of the modified surface and its influence on overall column efficiency, stability and neutrality. Surfaces modified with trimethylchlorosilane^{2,9}, hexamethyldisilazane⁹⁻¹¹, polydimethylsiloxane⁴, and octamethylcyclotetrasiloxane^{5,6,12} have been characterized using techniques such as cross-polarization magic angle spinning (CP-MAS) NMR and ¹H NMR spectroscopy, reflectance and normal IR spec-

troscopies, capillary gas chromatography (GC), GC-mass spectrometry (MS), scanning electron microscopy, secondary-ion mass spectrometry, electron spectroscopy for chemical analysis and capillary rise measurements.

PMHS-modified siliceous surfaces have been described as having high water contact angles¹³⁻¹⁵, high thermal stability¹³, stable bonds with the surface^{8,13}, and stability under aqueous treatments^{15,16}. The purpose of this study was to determine the characteristics of the PMHS-modified fused-silica capillary surface and to form a composite description of the deactivated surface. The characteristics determined include film neutrality, inertness, thickness, efficiency, non-extractability, thermal stability, polarity, Si-H content, surface tension, and bonding to the silica surface. The instrumental methods used were capillary GC and Fourier transform infrared (FT-IR) spectroscopy. The composite description of the deactivated surface provides evidence to explain why the PMHS deactivation-modification method is an attractive alternative to the higher temperature methods.

EXPERIMENTAL

Materials

A mixture of linear and cyclic polymethylhydrosiloxanes (PMHS, 85 centistoke fluid) and pentamethylhydrodisiloxane (PMDS) were obtained from Petrarch Systems (Bristol, PA, U.S.A.). Trimethylhydrosilane (TMS) gas was obtained from PCR Research Chemicals (Gainesville, FL, U.S.A.) in pressurized cylinders. Triphenylsilanol (TPS) was obtained from Silar Labs. (Scotia, NY, U.S.A.). The purities of TPS and PMDS were evaluated by capillary GC and found to be greater than 99%. Therefore, compounds were used as received from the supplier, without further purification.

Fused-silica capillary tubing of 320 and 200 μm I.D. (Hewlett-Packard, Avondale, PA, U.S.A.) and amorphous fused silica (Cab-O-Sil, grade M-5, Cabot, Tuscola, IL, U.S.A.) were the siliceous support materials used.

Preparation and testing of capillary columns

Specific column treatments are recorded in Table I. Pretreatments with distilled/deionized water, hydrochloric acid (6 *M*), and nitrogen gas purges are indicated. Final temperatures and times of the pretreatments are also indicated; the initial temperature for all treatments was 40°C with a program rate of 8°C min⁻¹. The deactivation reagent was dynamically coated neat or statically coated to give specific film thicknesses as noted. The term "neat" indicates a dynamic coating of a 10-25% column volume plug of neat reagent at 2-10 cm s⁻¹ with a 5 m \times 200 μm I.D. buffer capillary at the end. Capillaries purged with TMS gas for 15 min were flame sealed and heat treated in a similar fashion. In all cases, the capillaries were heated from 40°C to the final temperature at a rate of 8°C min⁻¹. The deactivation atmosphere indicates the gas used to purge the column of traces of oxygen. Coated capillaries were purged for 15-45 min with inert gas before being flame sealed. The dynamic deactivation method (simultaneous purging and heating) is denoted by "N₂ purged". All columns (except columns 7-9) were rinsed with 5-10 ml of dichloromethane after the deactivation heat treatment. Columns 7-9 were initially left unrinsed to insure reliability in the thickness of the coated PMHS phase.

TABLE I
FUSED-SILICA CAPILLARY COLUMN DEACTIVATIONS

Column No.*	Dimensions [I.D. (μm) \times length (m)]	Column** pretreatment	Deactivation reagent	Deactivation conditions	Deactivation atmosphere
1	320 \times 10	—	PMHS, neat	300°C/6 h	N ₂
2	320 \times 4	—	PMHS, neat	300°C/4 h	N ₂
3	320 \times 4	N ₂ , 280°C/36 h	PMHS, neat	300°C/4 h	N ₂
4	320 \times 4	N ₂ , 280°C/36 h	PMHS, neat	300°C/4 h	N ₂
5	320 \times 4	H ₂ O/N ₂ , RT/6 h N ₂ , 280°C/36 h, HCl/N ₂ , RT/1 h	PMHS, neat	300°C/4 h	N ₂
6	320 \times 4	—	—	—	—
7	320 \times 4	—	PMHS, 0.0025 μm	250°C/0.5 h	N ₂ purged
8	320 \times 4	—	PMHS, 0.025 μm	250°C/0.5 h	N ₂ purged
9	320 \times 4	—	PMHS, 0.25 μm	250°C/0.5 h	N ₂ purged

* Each column in this table represents two experimentally prepared columns.

** Treatments refer to: N₂ = purge with N₂ gas, H₂O/N₂ = purge with N₂ bubbled through H₂O, HCl/N₂ = purge with N₂ bubbled through 6 M HCl, and RT = room temperature.

Hydroxylation of fused-silica capillaries was accomplished according to Neu and Heeg¹⁷, but at only 350°C for 4 h. Following hydroxylation, these capillaries were purged with trimethylhydrosilane gas for 15 min, after which their ends were sealed and the capillaries heated from 40°C, at 8°C min⁻¹, up to 300°C and held for 4 h. These columns were rinsed with 5–10 ml of dichloromethane and statically coated with 0.25- μm films of SE-54. They were then evaluated with a Carlo-Erba 4160 gas chromatograph equipped with cold on-column injection and flame ionization detection (FID). The hydrogen carrier gas linear velocity was maintained at 40 cm s⁻¹ with split ratios of 100:1. The solute test mixtures used to evaluate capillary surface neutrality and inertness were similar in composition and concentration to those used earlier⁷. All chromatograms were obtained at a 2–5-ng full-scale response for alkanes (1 \times 10⁻¹¹ A f.s.). Basic and acidic polarity tests were run at 40°C and, after a 2-min isothermal period, programmed at 4°C min⁻¹ up to 160°C.

Some deactivated capillaries were statically coated with a 0.25- μm film of SE-54 (Applied Science, State College, PA, U.S.A.) and evaluated. All other deactivated capillaries were evaluated (uncoated) as post-columns connected to a coated column via a zero dead-volume butt connector. These columns were evaluated under the same conditions described above, except that split injection (250°C) was used.

A Hewlett-Packard 5890 gas chromatograph was used in determining capacity factors, column efficiency, and maximum column bleed. Split injection at 180°C and FID (250°C) were used at a hydrogen carrier gas velocity of 90 cm s⁻¹ and a split ratio of 50:1. Using the latter chromatographic conditions, PMHS coated capillaries deactivated at 300°C for 4 h and rinsed with 5–10 ml of dichloromethane were successively heated to 250, 275, 300, 325 and 350°C at 4°C min⁻¹ and held for 30 min while the maximum column bleed was recorded. Capacity factors were obtained for normal alkanes injected on 40°C isothermally controlled PMHS deactivated columns,

and at 100°C for the same columns coated with a 0.25- μm film of SE-30 (Applied Science).

FT-IR analysis of the reaction of PMDS on Cab-O-Sil

Fumed silica (Cab-O-Sil) was dehydrated by heating it to 280°C for 6 h under a purge of nitrogen gas. PMDS (0.502 g), dissolved in 30 ml of *n*-pentane, was mixed with dried Cab-O-Sil (1.978 g), stirred, and sonicated slightly to a homogeneous slurry. The solvent was driven off overnight by a gentle nitrogen purge at room temperature. A 0.20-g portion of coated Cab-O-Sil was then placed in a borosilicate test tube (90 mm \times 6 mm I.D. \times 7 mm O.D.), purged lightly with N₂ for 5 min, and flame sealed. After programmed heating from 40°C, at 8°C min⁻¹, to 300°C for 4 h, the test tube was opened and 30 mg of the Cab-O-Sil were pressed into a 0.2-mm thin, transparent wafer in a die press (10 tons pressure) for 5–10 s.

The wafers were analyzed with a Sirius 100 FT-IR spectrometer (Mattson Instruments, Madison, WI, U.S.A.) equipped with a deuterated triglycine sulfate (DTGS) detector. Fifteen scans were made with an iris area of 1.22 cm².

RESULTS AND DISCUSSION

The characteristics of the PMHS deactivation film on the fused-silica capillary column surface were expected to be similar to those of the hydrophobic films previously described from the reaction of PMHS on glass surfaces^{13–16}. The hydrophobic films on glass had a low surface tension (high water contact angle)^{13–15} and were very thin¹³. The bonded and cross-linked films were also characterized as solvent non-extractable^{13–15} and thermally stable up to 350–400°C^{13,16}. Such surface-bonded, cross-linked, hydrophobic films provided initial evidence of the nature of the PMHS deactivation film on fused-silica capillary columns.

Reaction of PMHS within fused-silica capillaries produces a surface that is neutral and inert. Fig. 1 illustrates the typical chromatographic performance of a deactivated and coated capillary, tested with solutions of acidic and basic probes at 2–4 ng per solute. Aliphatic primary amines eluted without tailing and with good efficiency. The deactivated surface was clearly neutral, as attested by the accompanied fine peak shapes and heights of the alcohol, diol, and acidic phenols. This column served as the standard by which all other deactivated, uncoated capillaries were compared. The reproducibility of this deactivation was shown to be as high as the degree of achieved neutrality and inertness.

The influence that contaminants, adsorbed on untreated fused-silica surfaces, had on the deactivation film was studied. The major fused-silica innerwall contaminants are physically adsorbed water and acidic compounds, such as hydrochloric acid and nitric acid^{18,19}. Columns 2–5 were dehydrated, rehydrated, and re-acidified in various combinations, as listed in Table I, then reacted with PMHS. Surprisingly, all of these PMHS-modified capillaries were well deactivated and gave neutral and inert surfaces such that no ranking of the pretreatments could be made. This can be attested by the similarity of the chromatograms obtained on several of these capillaries shown in Fig. 2 when connected after the well-deactivated column 1. The slight tailing of the aliphatic amine peaks was likely due to a systematic error from surface activity in the column connection. However, it is recommended that for long-term

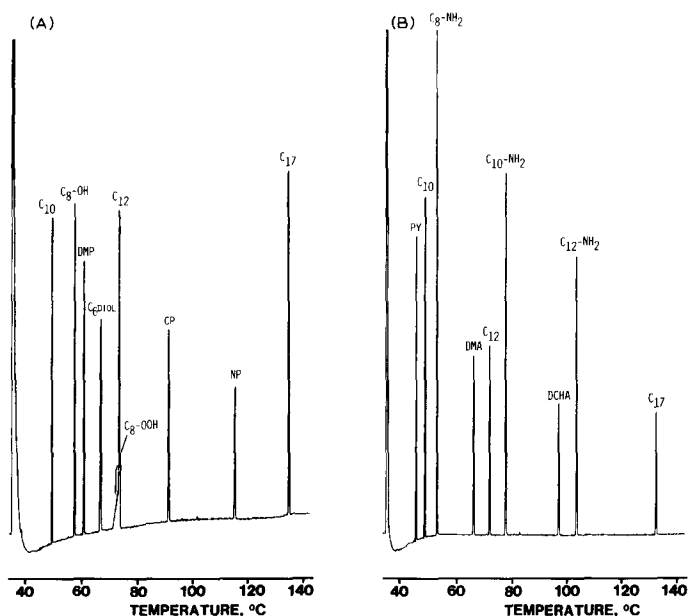


Fig. 1. Gas chromatograms of (A) acidic and (B) basic test mixtures on a 23 m \times 320 μ m I.D. PMHS-deactivated, SE-54 coated (0.25 μ m film thickness) column. Conditions: H₂ carrier, 40–140°C at 4°C min⁻¹, 5 ng full scale deflection. Solutes represented by labeled peaks are: C₁₀ = *n*-decane, C₈-OH = 1-octanol, DMP = 2,6-dimethylphenol, C₆-diol = 1,6-hexanediol, C₈-OOH = octanoic acid, C₁₂ = *n*-dodecane, CP = 2,4,5-trichlorophenol, NP = 4-nitrophenol, C₁₇ = *n*-heptadecane, PY = 3,5-dimethylpyridine, C₈-NH₂ = 1-octylamine, DMA = 2,6-dimethylaniline, C₁₀-NH₂ = 1-decylamine, DCHA = N,N-dicyclohexylamine, C₁₂-NH₂ = 1-dodecylamine.

stability of the deactivated and coated column, that the expulsion of hydrochloric acid via nitrogen purging at elevated temperature precede the coating and deactivation with PMHS.

The four deactivated capillaries (columns 2–5) also produced lower capacity factors (Table II) than the untreated surface (column 6). The different aqueous and acidic conditions tested did not significantly influence the final film thicknesses of the PMHS-modified surfaces. At the onset of the experiment, it was thought that PMHS deactivation in the presence of large amounts of physically adsorbed water should produce thick deactivation films due to a high incidence of cross-linking achieved chiefly through Si–H hydrolysis–dehydrocondensation¹⁴. However, the capacity factors obtained on columns 4 and 5 were found to be identical to those obtained on the dehydrated surface of column 3. Apparently, hydrolysis–dehydrocondensation of silylhydrides by physically adsorbed water initially occurs at the interface between the surface adsorbed water and PMHS, and then continues into the bulk liquid and gaseous PMHS oligomeric phases. Such reactions effectively increase both depolymerization via hydrolytic siloxane cleavage to form low-molecular-weight cyclics and polymerization via hydrolysis–dehydrocondensation (cross-linking). Such simultaneous decrease and increase in polymer molecular weight distributions have been observed by analytical gel permeation chromatography of the reagent rinsed out of

TABLE II
CAPACITY FACTORS (k') OF *n*-ALKANES ON TREATED CAPILLARIES
Mean capacity factors from 5 determinations at 40°C are given.

Alkane	Column number								
	2	3	4	5	6	7	8	9	
C ₁₃	3.2	2.5	2.6	2.4	6.8	5.0	10.1	500	
C ₁₄	8.2	6.6	6.6	6.4	17.4	12.8	27.3	1270	
C ₁₅	20.4	16.4	16.6	15.8	44.8	32.1	72.4	2470	
Film thickness (μm)	<0.001	<0.001	<0.001	<0.001	0.000	0.0025	0.025	0.25	

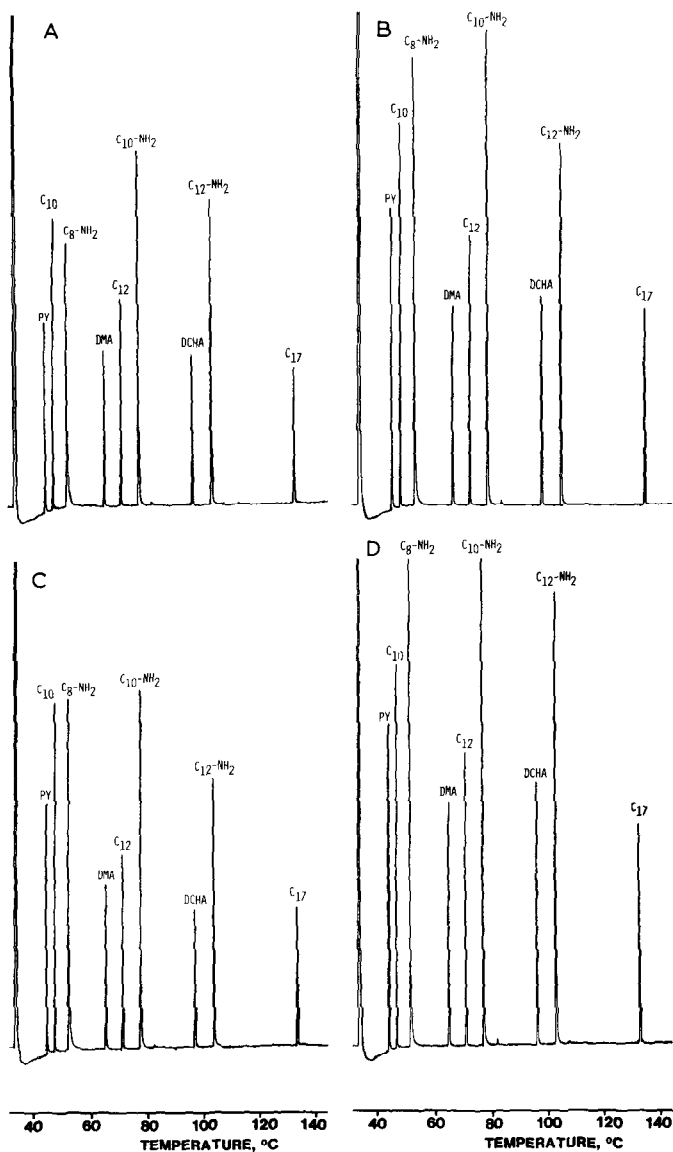


Fig. 2. Gas chromatograms of the basic test mixture on columns with varying water and acid pretreatments. Column 1 used as separation pre-column with: A = column 2, B = column 3, C = column 4, D = column 5 as uncoated post columns. Conditions and peaks as in Fig. 1.

phenyl-substituted PMHS-deactivated capillaries. It is presumed that through these processes, there is no net increase in the siloxane deactivation film thickness.

The film thicknesses of the PMHS-deactivated columns²⁻⁵ were estimated from the capacity factors listed in Table II, assuming the same decreasing relationship between capacity factors and film thickness as was found from the known 0.25-

0.0025- μm film thicknesses (columns 7–9). The capacity factors from columns 2–5 were one-half and one-fourth of those obtained from columns with 0.0025- μm (column 7) and 0.025- μm (column 8) film thicknesses, respectively. A maximum 10-fold decrease in film thickness from 25 Å (column 12) to 2.5 Å (columns 7–10) supports the idea of a near monolayer film. Even figuring a direct (1:1) capacity factor–film thickness relationship, then one-half of 0.0025 μm brings the film thickness to a maximum of only 13 Å. This calculated deactivation film thickness corresponds to a deactivation film ranging from 1–4 monolayers; a contribution of less than 0.5% to the normal stationary phase film thickness (0.25 μm). The chromatographic efficiencies of these deactivated columns, coated with SE-30 are listed in Table III. Notice that the coated column efficiencies for PMHS-deactivated capillaries (columns 2–5) were similar to the efficiency of the non-deactivated SE-30 coated capillary (column 6). Therefore, when coated with stationary phase, the influence of the PMHS deactivation film thickness on solute retention is negligible, while column efficiency increases slightly.

TABLE III

TOTAL THEORETICAL PLATES FOR PMHS-DEACTIVATED SURFACES COATED WITH A 0.25- μm FILM OF SE-30

Mean total theoretical plates from 5 determinations at 100°C are given and 95% confidence limits were ± 100 for each column.

Alkane	Column number				
	2	3	4	5	6
C ₁₄	5900	5500	5700	5900	5500
C ₁₅	6700	6500	6800	6400	6400

The PMHS-modified surface was shown to be non-extractable with organic solvents and exhibited high thermal stability. The PMHS-modified surfaces, rinsed of non-surface bonded reagent with dichloromethane, produced a maximum column bleed of only 0.2 pA at 250°C, 0.7 pA at 300°C, 0.8 pA at 325°C, and 1 pA at 350°C. The capacity factor calculated for *n*-tetradecane (obtained at 40°C after each successive heating) decreased from 10.3 at room temperature to 8.5 at 300°C and 7.1 at 350°C. Columns deactivated with PMHS at 300°C and coated with SE-33 and SE-54 have been routinely used to 300°C without noticeable column bleed, peak shape deformity, or decrease in column efficiency. Earlier studies have reported that the water contact angle of a PMHS film on glass was markedly reduced only after heat treatments above 350°C¹³ and 400°C²⁰. The PMHS deactivation film is, therefore, stable under normal chromatographic conditions for columns coated with polydimethylsiloxane stationary phases.

The degree of deactivation, and hence the surface polarity, achieved after various aqueous and acidic pretreatments was evaluated using retention indices of some basic and acidic solutes. Listed in the first three rows of Table IV are retention indices obtained on deactivated capillaries 2–5 and on a non-deactivated capillary 6 con-

TABLE IV

KOVATS' RETENTION INDICES OF VARIOUSLY PRETREATED PMHS-DEACTIVATED COLUMNS

Retention indices at 95% confidence limits of the mean from 4 determinations on each column.

Column number and treatment*	C_8-NH_2	$C_{10}-NH_2$	C_8-OH	NP
1	1038 ± 1	1248 ± 1	1069 ± 2	1543 ± 2
2-5	1040 ± 1	1251 ± 1	1069 ± 1	1546 ± 1
6	1184 ± 1	1351 ± 1	1077 ± 1	1549 ± 1
3, treated with H ₂ O/N ₂ , 280°C/30 min	1040 ± 1	1251 ± 1	1069 ± 1	1546 ± 1
H ₂ O/N ₂ , 350°C/4 h, SE-54, 0.25- μ m film thickness	1299 ± 2	1419 ± 1	1115 ± 2	1550 ± 1
H ₂ O/N ₂ , 350°C/4 h, TMS, 300°C/4 h, SE-54, 0.25 μ m film thickness	1125 ± 1	1305 ± 1	1056 ± 1	1515 ± 1

* Treatments refer to: H₂O/N₂ = purge with N₂ bubbled through water, TMS = deactivated with trimethylhydrosilane gas at 300°C/4 h.

ected to column 1. Comparison of retention indices (ΔRI) of the two aliphatic amines obtained on the non-deactivated surface to those on the deactivated surfaces ($\Delta RI > 100$) illustrates best the blockage of acidic surface silanols by PMHS. The retention indices of the two acidic compounds did not decrease as much upon deactivation of surface silanols since the surface was originally acidic. Retention indices from capillaries 2-5 showed little deviation from the mean values, again illustrating the reproducibility of complete surface silanol deactivation regardless of slight differences in the pretreatment of the capillary surface.

The deactivation film showed no evidence of remaining Si-H bonds. The neutrality of the PMHS-deactivated surface did not change after being purged with water-saturated nitrogen gas at 280°C for 30 min (Table IV, fourth row). Had any significant proportion of silylhydride bonds remained on the deactivation film, a significant decrease in retention indices for these compounds would have been obtained after such a hydrolytic treatment. In addition, TPS was found to react with silylhydride bonds, with the major portion (70-80%) being reduced to triphenylhydrosilane⁸. However, no triphenylhydrosilane could be detected by capillary GC or by FT-IR spectroscopy from concentrated extracts of TPS which had been coated and heated on untreated fused-silica surfaces or on PMHS-deactivated surfaces. Regardless of the mechanism, these evidences support the idea that no silylhydride bonds remain on the deactivated surface after the solvent rinsing step that follows heat treatment of the PMHS-coated capillary.

The difference in the polarity of the silylhydride bond ($Si^{\delta+}-H^{\delta-}$) and the Si-CH₃ appendage ($C^{\delta-}-H^{\delta+}$) was also used to obtain further evidence of the insignificance of the proportion of unreacted silylhydrides on the PMHS deactivated surface. The purposeful presence of Si-H bonds on PMHS-coated column 9 increased the average retention indices of 1-aminooctane and 1-aminodecane to 1447 and 1610, respectively, which was well above the retention indices for the same compounds obtained on column 1 in Table IV. In fact, the retention indices for the compounds

listed in Table IV for columns 1–5 are (with 95% confidence) equal to those obtained on octamethylcyclotetrasiloxane-deactivated columns. It can, therefore, be concluded that there is not an abundance of unreacted silylhydrides remaining on PMHS-deactivated capillary surfaces. The methyl groups project out from the deactivation film, providing a high water contact angle of 80–90°^{13–15} and a critical surface tension of 20 mN m⁻¹ (ref. 21). The critical surface tension (20 mN m⁻¹) and relative surface coverage (Zisman plot slope of $-35 \times 10^{-3} \text{ mN}^{-1}$) of the PMHS-deactivated film is similar to corresponding values for high temperature (400°C) reactions of octamethylcyclotetrasiloxane, trimethylchlorosilane + hexamethyldisilazane, and polydimethylsiloxane on glass and fused-silica capillaries²². Any unreacted silylhydride bonds would have increased the critical surface tension and relative retention of chromatographed primary amines.

Evidence for the bonding of the PMHS deactivation layer to the fused-silica capillary surface was obtained using model compounds and surfaces. The bonding characteristics of PMHS and other organosilicon hydrides to siliceous surfaces via dehydrocondensation has been well established^{13–15}. Supplementary experiments were performed for confirmation only.

One of the first confirmations for bonding of PMHS to the surface came with deactivations with gaseous TMS. Hydroxylation of fused-silica capillaries gave rise to silanol rich surfaces on which even 2,6-dimethylphenol and 2,6-dimethylaniline peaks showed great evidence of reversible adsorption. More basic and acidic compounds eluted with remarkably high retention, as noted by the data in the fifth row of Table IV. However, when the same surface hydroxylation was followed by treatment with TMS, all solutes, including primary amines, eluted with corresponding decreases in relative retention. Similar results have been obtained with trimethylchlorosilane and hexamethyldisilazane^{9–11}. Many of the surface silanols dehydrocondensed with the reactive TMS gas while others were merely covered by the umbrellas of resultant surface-bonded trimethylsiloxy groups.

Surface bonding was also observed from reaction of monohydridic silanes and siloxanes on siliceous materials¹⁵. The FT-IR spectra in Fig. 3 show that after reaction at 300°C for 4 h and multiple dichloromethane rinses, methyl groups of pentamethyldisiloxane still remained, as evidenced by the C–H absorbance bands at about 2950 cm⁻¹. No absorbance at 2180 cm⁻¹ indicated the absence of Si–H bonds and indicated that the methyl group absorption was due to bonded pentamethylsiloxy groups and not from the unreacted reagent. The concomitant reduced absorbances of physically adsorbed water (3400–3500 cm⁻¹) and free silanols (3750 cm⁻¹) indicated their reaction with the Si–H bond of the monohydridic disiloxane. PMDS had dehydrocondensed with surface silanols, forming a permethylsilylated surface physically similar to other descriptions¹⁵ and showing no evidence of Si–H bonds on the modified silica surface. Methylsilicone hydrides (including PMHS) do dehydrocondense with silica surface silanols to bond the methylsiloxane species to the support surface.

Thermally-initiated hydrolysis of Si–H bonds of PMHS by capillary wall adsorbed water to form Si–OH groups, followed by silanol–silanol condensation or silanol dehydrocondensation with available Si–H bonds complements the surface silanol bonding dehydrocondensation reaction with PMHS. Hydrolysis of Si–H bonds and subsequent condensation or dehydrocondensation leads to a resinous

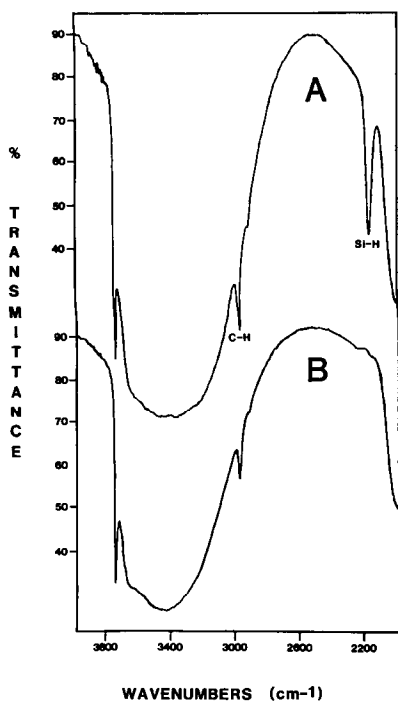


Fig. 3. FT-IR spectra of pentamethylhydrodisiloxane coated on Cab-O-Sil. Spectrum A: room temperature; spectrum B: after reaction at 300°C for 4 h and dichloromethane wash.

polymer covering of the fused-silica surface. Surface silanols then anchor this PMHS cross-linked film to the column wall via dehydrocondensation. Together, these two reactions produce a cross-linked and surface-bonded methylpolysiloxane film void of silylhydride bonds. This deactivation film is characterized as being very thin (1–4 monolayers), bonded to the surface via siloxane linkages, cross-linked into a dense network with methyl groups protruding upwards from the surface, containing no exposed Si–H bonds, non-extractable by organic solvents, and thermally stable to at least 300°C.

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