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SURFACE-BONDED SILICONES FROM VOLATILE MONOMERS FOR CHROMATOGRAPHY*

CORAZON R. HASTINGS** AND WALTER A. AUE***

University of Missouri, Columbia, Mo. 65201 (U.S.A.)

AND

JOSEPH M. AUGL

Naval Ordnance Laboratories, Silver Spring, Md. 20910 (U.S.A.)

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SUMMARY

In an earlier report[12] we have described a multistage process which produces silicones polymerized on, and chemically bonded to, chromatographic supports. While only monomers of low volatility could be used at that time, we have now modified the process to accommodate highly volatile starting materials. Di- and trifunctional compounds of different polarity could be partially hydrolyzed in solution and subsequently polymerized in fluidized bed. The resulting phases were characterized by gas–liquid chromatography in terms of column bleed, solute retention and resolution; by liquid phase extractability, by thermogravimetric analysis, and C, H analysis. Most of the phases showed virtually complete surface bonding and bleed comparable to chromatography-grade SE-30. Resolution and retention time of various solutes appeared related to liquid phase cross-linking and substituent carbon chain length. Plate numbers generally improved, and retention times increased, through secondary heat treatments. The developed phases have been utilized in typical gas–liquid chromatographic separations.

INTRODUCTION

The modification of solid surfaces by chemical or physical bonding of organic substances is a subject which bridges traditional areas of research. It is of considerable importance in the industrial areas of protective coatings and reinforced plastics and the academic fields of surface chemistry and chromatography.

For most applications, stable chemical bonding would represent the ideal solu-

tion, but it is usually hard to achieve. The question: chemical bonding — yes or no? has been asked in many instances. Numerous studies on the nature of glass–resin interfaces are a case in point (*e.g.* refs. 1, 2, 3).

In the area of chromatographic techniques, two directions of research can generally be distinguished. The first, the older and predominant one, concerns the modification of surfaces vaguely in the range of an incomplete monomolecular layer. The purpose of these investigations is manifold: physicochemical characterization of surfaces, gas–solid chromatographic separation, surface deactivation for subsequent use in gas–liquid chromatography (GLC) and the like. A review listing works in some of these areas has recently appeared[6]. Of perhaps special importance in the context of this paper are results by the groups of OTTENSTEIN, PURNELL, KISELEV, KREJCI, and others (compare ref. 7).

The second field, younger and of considerable recent prominence, concerns the modification of surfaces with liquid layers of greater thickness, similar to regular GLC phases, but chemically bonded to the surface. These materials are designed for use in partition chromatography with either gas or liquid used as mobile phase. The "brushes" of HALASZ AND SEBASTIAN[8,16,17] are the best-known example. Another surface-bonded carbon-based polymer was reported by MOORE AND DAVISON[9].

The first attempt in chemically bonding silicone liquid phases to solid supports was carried out by ABEL *et al.*[10], who polymerized hexadecyltrichlorosilane on Celite. GROB[11] tried similar procedures for glass capillaries.

In our first study on surface-bonded silicones, we used a variety of di- and trichlorosilanes, neat and in mixture, to produce liquid phases on diatomaceous earth or silica gel supports, and glass or porous silica beads. Some of these phases were virtually non-removable by exhaustive extraction and showed good chromatographic performance in terms of thermal stability, HETP and peak symmetry of polar compounds[12]. Liquid phase loading can reach 40 % and such materials can also be used for the collection of air pollutants[13].

Recently, KIRKLAND AND DeSTEFANO[14] of DuPont and FILBERT AND EATON[15] of Corning reported on the polymerization of silanes on "controlled surface porosity support" and "controlled-pore glass particles", respectively. Modification of porous glass for GC was also studied by WOLF AND HEYER[18]. AL-TAIAR *et al.*[7] mixed silicontetrachloride with silicone monomers, hydrolized and ground the resulting material for use in a gas chromatograph–mass spectrometer unit.
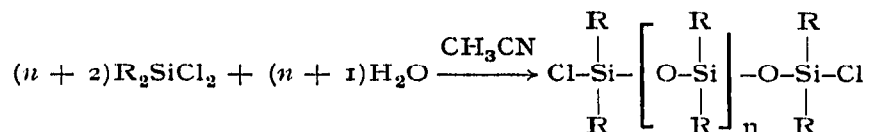
In this present study, we used Chromosorb G exclusively as a support and investigated the effects of silicone monomer structure. In previous work[12], we had used only monomers of relatively low volatility to produce the desired coatings. Both in industrial usage and chromatographic applications, however, silicones derived from highly volatile monomers dominate. We considered it therefore highly desirable to investigate such compounds as starting materials for chromatographic phases.

The most important step in our synthesis of surface-bonded silicones is the polymerization in fluidized bed[12]. The amount of monomer lost from the coated particles to the carrier gas is negligible with compounds such as octadecyltrichlorosilane. With compounds of high vapor pressure, however, serious if not complete loss can result.

The situation is aggravated by the particular conditions which are desirable in the polymerization process. In general, the rate of water addition should be low and the temperature of the gas as high as proves compatible with other process

variables. Unfortunately, both of these conditions result in increased monomer loss.

Rather than to cool the reactor, recycle the carrier gas, or otherwise modify the fluidized bed polymerization, we decided to add a partial hydrolysis step to the process. In this step, water is added slowly to the halosilane solution in amounts sufficient to combine a small number of monomer units, for instance:

$$(n + 2)R_2SiCl_2 + (n + 1)H_2O \xrightarrow{CH_3CN} Cl-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-\left[O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}\right]_n-O-\underset{\underset{R}{|}}{\overset{\overset{R}{|}}{Si}}-Cl$$

where $n = 2$ in this paper.

Of course, the exact nature and distribution of the resulting compounds are unknown. The preferred products would be straight polysiloxane chains devoid of silanol groups. There is some reason to assume[19] that the reaction conditions chosen favor the formation of the desired structures.

Through partial hydrolysis, a decrease in volatility is achieved which permits the subsequent polymerization to be conducted in a fluidized bed at elevated temperature.

We have selected series of di- and trifunctional chlorosilanes according to high volatility and commercial availability, and not just according to expected GLC performance. Methyltrichlorosilane, for instance, could hardly be expected to yield a superior chromatographic phase. Dimethyldichlorosilane, on the other hand, is the monomer from which such common GLC phases as SE-30, DC-200, OV-1, OV-101, etc., are derived. In comparing the products formed from different monomers, it was important for us to notice any consistent change related to chemical structure, as for instance, in the methyl–ethyl–propyl–butyl series of trichlorosilanes.

There are quite a number of analytical techniques which can be mustered to characterize the produced materials. We have chosen criteria closely related to gas chromatographic performance, a main field of use for silicone coatings. Thus, we conducted (1) GLC bleed experiments, (2) plate height measurements, (3) exhaustive extraction, (4) chromatographies of test mixtures, (5) thermogravimetric characterization and (6) C, H analysis of the developed phases.

EXPERIMENTAL

(A) Synthesis of chromatographic phases

(1) *Treatment of the solid support.* Chromosorb G, 60/80 mesh, "non-acid washed" (Johns-Manville), is covered with conc. HCl and kept under gentle reflux for 24 h, decanting and replacing the acid once, approximately at half-time. After washing the diatomaceous earth with distilled water to neutrality, the remaining water is removed by several rinses with anhydrous acetone, followed by evaporation of the acetone in vacuum at 65°. The resulting material can be stored in a tightly stoppered bottle.

For the so-called "initial reaction"[12], 30.0 g of the acid-treated Chromosorb is poured into a solution of 10 ml methyltrichlorosilane (MTCS) in toluene (sufficient to cover the Chromosorb) and the mixture refluxed for 4 h under exclusion of atmospheric moisture. The excess MTCS and the toluene are evaporated in vacuum on

a 65° waterbath (this particular temperature is incidental) and the solid support is now ready for reaction with the partially polymerized halosilane.

(2) *Partial monomer hydrolysis*. To a magnetically stirred solution of halosilane(s) in 50 ml acetonitrile, a solution of water in 30 ml acetonitrile is added dropwise at room temperature and the mixture allowed to stand for 30 min. Permitting only a minimum of contact time with the atmosphere, the pretreated solid support (see above) is poured into the solution of partially hydrolyzed monomer and the solvent removed by rotary evaporation on a 65° waterbath.

For all reactions, the amount of halosilane is calculated to yield a 10.0 % "theoretical load", defined as one hundred times the weight of the polymer divided by the weight of Chromosorb + polymer. Three moles of water are used for four moles of halosilane. To preserve the integrity of this ratio, the acetonitrile is dried prior to the reaction over calcium sulfate. Typical amounts calculated for this procedure are shown in Table I.

(3) *Polymerization*. The dried materials are polymerized in a fluidized bed of air at 100–110°, with approximately 6–8 ml of water introduced per hour. Most polymerizations are complete after 30 h as indicated by a pH higher than 6. This measurement is made on a sample taken from the fluidized bed and suspended in a small amount of distilled water.

(B) *Characterization of chromatographic phases*

(1) *Extraction*. All polymerized materials were extracted exhaustively in a Goldfisch Extractor (Fischer Scientific Company, St. Louis, Mo.) with benzene for 16 h, to determine the loss caused by extraction of non-surface bonded polymer. This loss was added to the "actual load" (*i.e.* the percentage of polymer on the extracted phases, as determined by C, H analysis) to calculate the "initial load" (*i.e.* the percentage of polymer before extraction) in Table III.

The residual, surface-bonded material was used for all chromatographic and other tests.

(2) *Column efficiency, performance, and bleed rate*. The exhaustively extracted chromatographic materials, and 10 % GC grade GE-SE-30 coated on acid-washed Chromosorb G, 60/80 mesh, were packed into 0.5 m × 4 mm I.D. pyrex columns (Perkin-Elmer model 800). These columns were subjected to the following consecutive

TABLE I

PARTIAL MONOMER HYDROLYSIS

Monomer	g monomer	g water
CH_3SiCl_3	7.522	0.679
$C_2H_5SiCl_3$	6.731	0.556
$C_3H_7SiCl_3$	6.222	0.473
$C_4H_9SiCl_3$	5.827	0.411
$CH_3(H)SiCl_2$	7.666	0.900
$(CH_3)_2SiCl_2$	5.808	0.607
$(C_2H_5)_2SiCl_2$	5.131	0.441
$(CH_3)_2SiCl_2$	4.014	0.559
+	+	
CH_3SiCl_3 (3:1 molar ratio)	1.549	

procedures: (a) Bring column temperature from ambient to 250° at a rate of 10°/min and then condition 16 h at 250° with a N_2 flow of 13 ml/min. (b) Chromatograph two test mixtures containing several types of organic structures; some of them typical
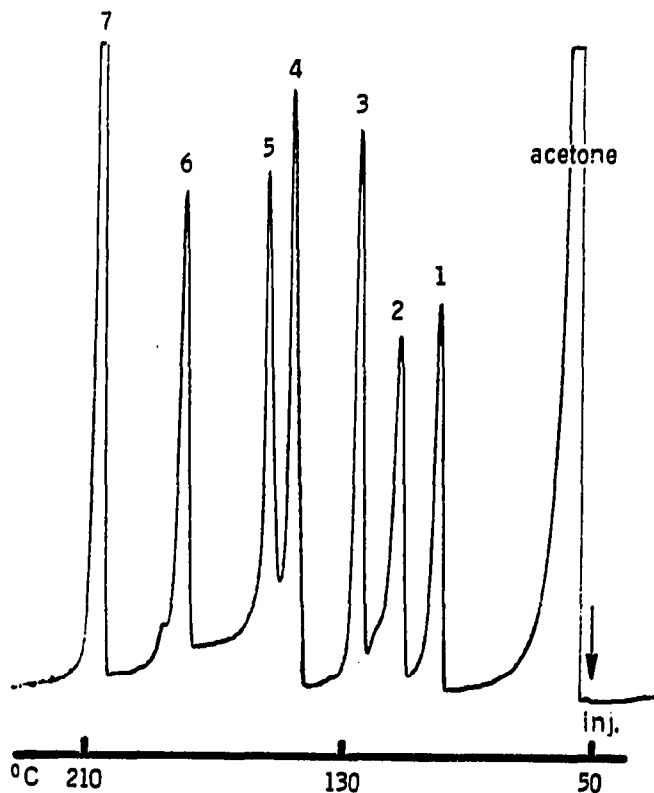

Fig. 1. Column, $[CH_3(H)SiO]_n$ (3.65 w% $(CH_3SiO_{3/2})_n$, see text) on 60/80 Chromosorb G, 0.5 m × 4 mm I.D. glass (Perkin-Elmer model 800). Initial temperature, 50°, 10°/min; N_2 flow rate, 13 ml/min. 1 = phenol; 2 = di-n-butylamine; 3 = ethylaniline; 4 = octanoic acid; 5 = p-toluic acid; 6 = dodecyl alcohol; 7 = methyl myristate.

TABLE II

EFFECT OF HEAT TREATMENT ON COLUMN EFFICIENCY

Monomer	% actual load[a]	HETP-250[b]	HETP-350	HETP-400 (cm)
CH_3SiCl_3	9.4	5.14	9.62	5.65
$C_2H_5SiCl_3$	6.5	0.14	0.08	0.08
$C_3H_7SiCl_3$	6.5	0.07	0.08	0.04
$C_4H_9SiCl_3$	5.4	0.07	0.05	0.05
$CH_3(H)SiCl_2$	7.9	0.21	0.13	0.11
$(CH_3)_2SiCl_2$	4.4	0.16	0.11	0.10
$(C_2H_5)_2SiCl_2$	0.4	0.68	0.57	0.63
$(CH_3)_2SiCl_2$ + CH_3SiCl_3 (3:1 molar ratio)	6.3	0.24	0.23	0.21
SE-30	9.6	0.11	0.10	0.10

[a] The polymer load of the extracted phases as determined by C, H analysis.
[b] All HETP values were measured at 6.5 ml/min N_2 and 190° with hexadecane.

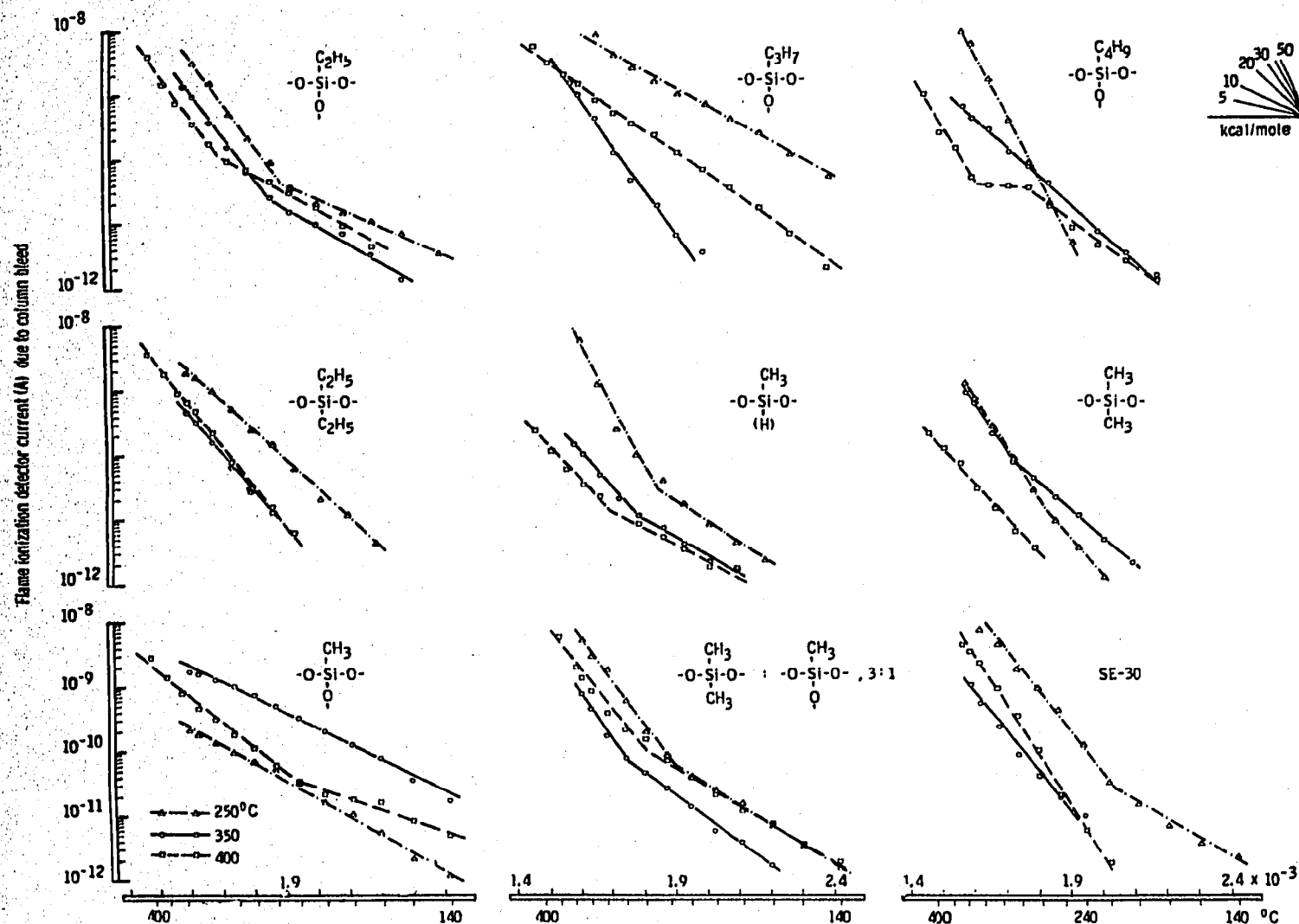Flame ionization detector current (A) due to column bleed

Fig. 2. Plot of log column bleed vs. $1/T$.

problem compounds such as phenols, acids, and amines. (A characteristic chromato-gram is shown in Fig. 1, taken from step g below.) (c) Chromatograph a solution of hexadecane in pentane at 190° and a N_2 flow of 6.5 ml/min to obtain the HETP after the 250° heat treatment, called "HETP-250" in Table II; and the hexadecane retention time shown in Fig. 8. (d) Temperature-program (starting at the highest sensitivity and attenuating as required) at 4°/min from 50° to 350° and a N_2 flow of 6.5 ml/min, to determine the bleed rate after the 250° heat treatment, called "250" in the bleed diagram (Fig. 2). (e) Repeat steps b and c (to check for a possible deteri-oration of the liquid phase). (f) Condition at 350° for 3 h at a N_2 flow of 13 ml/min, and repeat steps b, c, and d, to determine performance, column efficiency, and bleed rate (called "HETP-350" in Table II, and "350" in Fig. 2, respectively). (g) Condition at 400° for 1 h at a N_2 flow of 13 ml/min, and repeat steps b, c, and d, except that the column bleed is measured up to 400°. ("HETP-400" and "400".)

(3) *Other GLC tests.* After the column efficiency and bleed rate studies as de-scribed above, the columns were used to chromatograph a mixture of equal weights
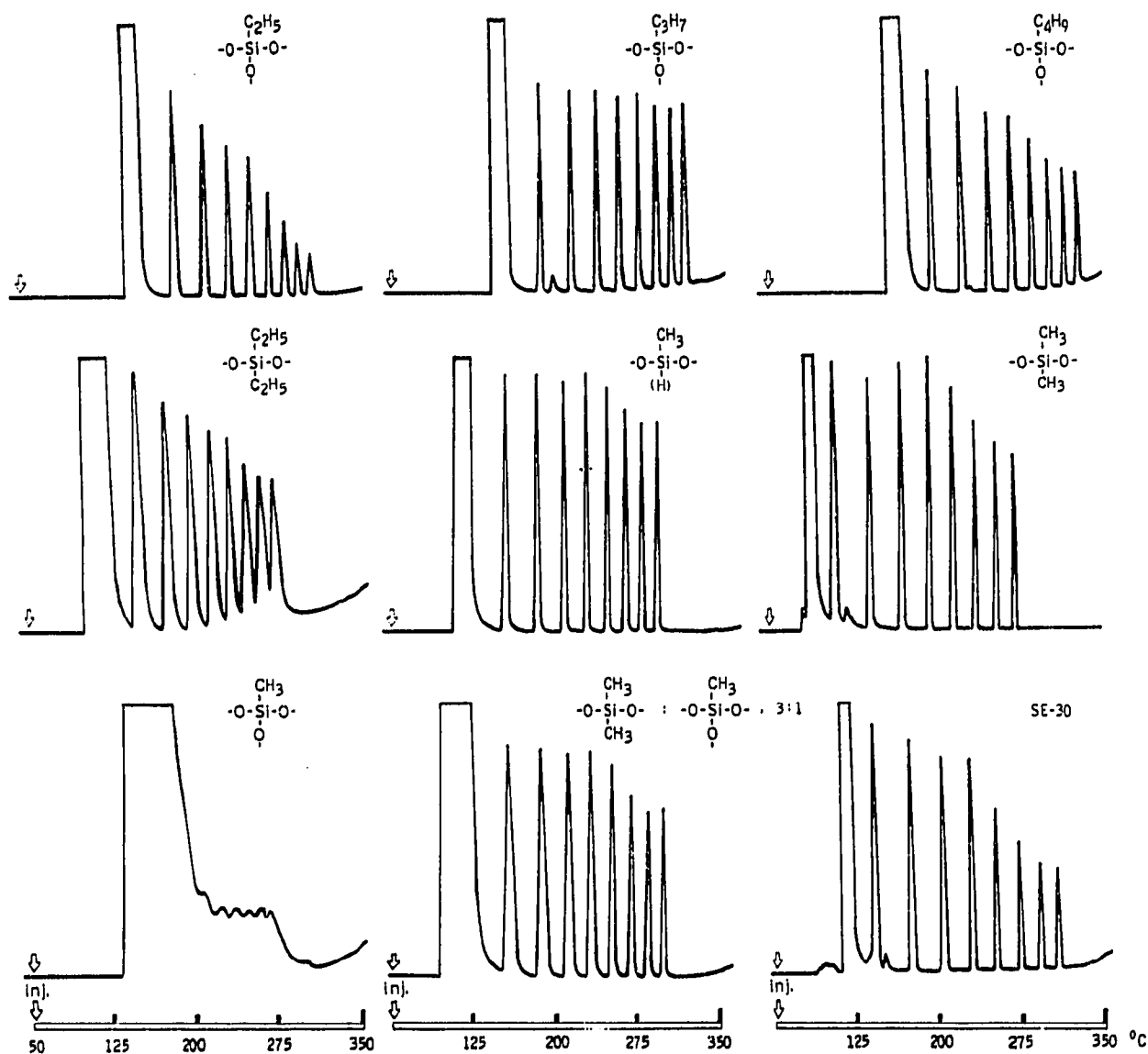
Fig. 3. Chromatogram of equal weights C_{10} through C_{24} even-numbered hydrocarbons. Column, 0.5 m × 4 mm I.D. glass (Perkin-Elmer model 800). Initial temperature, 50°, 12°/min; N_2 flow rate, 6.5 ml/min.

of even-numbered hydrocarbons in ethylbenzene solution from C_{10} to C_{24} (Fig. 3).

Further, some of these packed columns were tested with a mixture of equal volumes of *n*-alcohols comprising ethanol, 1-butanol, 1-hexanol, 1-octanol, 2-octanol, 1-decanol, and 1-dodecanol (Fig. 4).

The Van Deemter plots of four supported-bonded columns and the standard GE-SE-30 columns were measured at 190° using 0.2 μl injections of 1 % hexadecane in pentane (Fig. 5).

A portion of the exhaustively extracted mixed phase from dichlorodimethyl-silane (DMCS) and MTCS was used to pack a 1.1 m × 4 mm I.D. pyrex column (MicroTek model MT-220). It was conditioned at 250° for 30 h, deactivated with several injections of 10 μl bis(trimethylsilyl)trifluoroacetamide (BSTFA) at 190°, and

again conditioned at 320° for 15 h. This column was then used to separate picogram amounts of chlorinated hydrocarbon insecticides using the Mikro Tek Ni-63 electron capture detector (Fig. 6).

(4) *Thermogravimetric analysis.* Portions of the initial, exhaustively extracted phases (paragraph B1, above), were dried for 16 h at 100° in oil pump vacuum and analyzed in vacuum on a Mettler thermobalance. Part of the same dried phases were
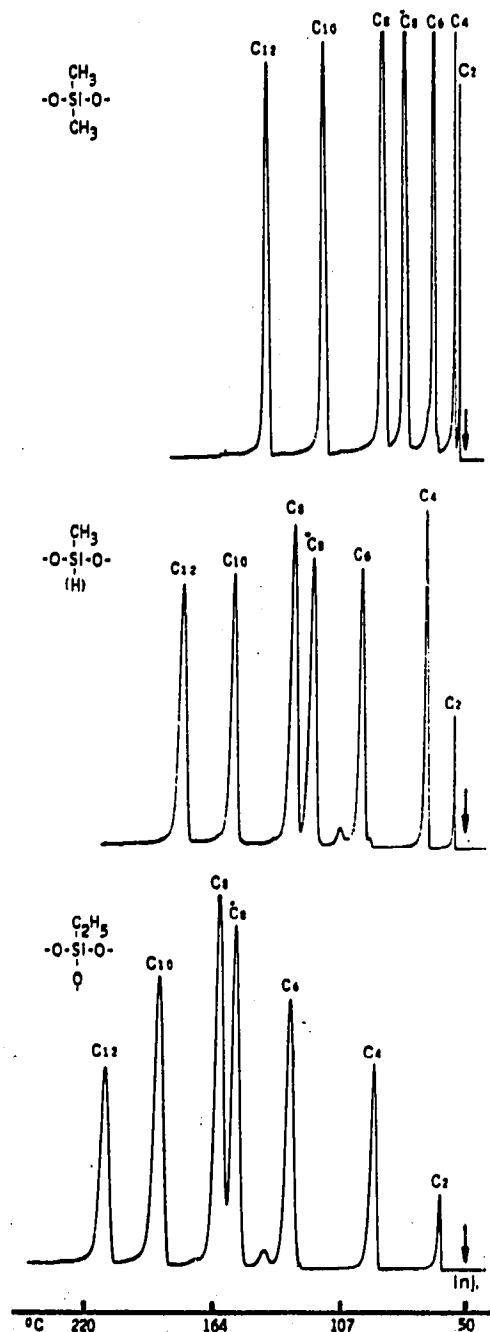
Fig. 4. Chromatogram of equal volume *n*-alkanol (1)s. Column, 0 5 m × 4 mm I.D. glass (Perkin-Elmer model 800). Initial temperature, 50°, 10°/min; N₂ flow rate, 13 ml/min. *2-octanol.

sent for C, H determination to Dr. F. KASLER at the University of Maryland (Table III).

RESULTS AND DISCUSSION

This study was designed primarily to show the feasibility of using silicone monomers of high volatility in an earlier described process[12], which yields support-bonded
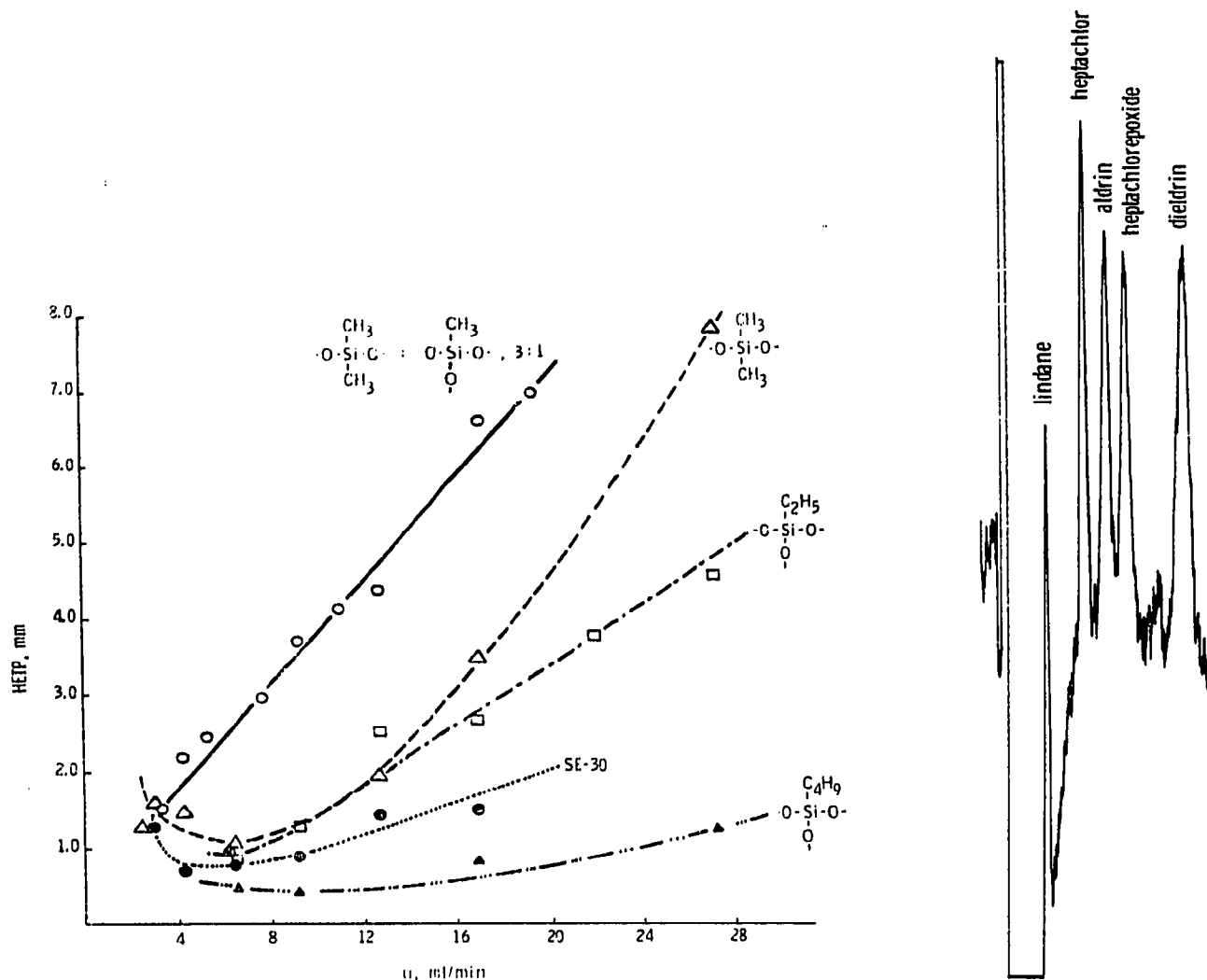

Fig. 5. GLC column efficiency (Van Deemter plot). 190°, hexadecane.

Fig. 6. Chromatogram of picogram amounts of chlorinated hydrocarbon insecticides. Column, 6.3 wt. % $[3(CH_3)_2SiO + CH_3SiO_{3/2}]_n$ on 60/80 Chromosorb G, 1.1 m × 4 mm I.D. glass. Oven temperature, 190°; N_2 flow rate, 33 ml/min. MicroTek model MT-220, Ni-63 detector, RF mode, 60 V, 240 μsec interval, 6 μsec width. Injected amounts, Dieldrin 2 × 10^{-12} g, all others 1 × 10^{-12} g.

liquid phases for chromatography. To avoid monomer losses in the heated fluidized bed, a partial hydrolysis was conducted prior to the polymerization, yielding still reactive products of much reduced volatility, i.e., chlorosiloxanes of one structure or another.

TABLE III

THERMO-GRAVIMETRIC ANALYSIS OF EXTRACTED PHASES

Monomer	% initial load[a,c]	% actual load[b]	Microanalysis[d] % found		TGA Before heat treatment			After heat treatment		
			C	H	% loss	Loss start (°C)	Half-life (°C)[e]	% loss	Loss start (°C)	Half-life (°C)[e]
CH_3SiCl_3	9.44	9.4	1.65	0.43	1.1	225	>760	0.6	680	>760
$C_2H_5SiCl_3$	6.55	6.5	1.94	0.40	4.0	225	530	3.5	345	615
$C_3H_7SiCl_3$	6.55	6.5	2.49	0.48	2.7	275	520	1.9	480	555
$C_4H_9SiCl_3$	5.60	5.4	2.16	0.48	3.0	235	505	2.1	435	545
$CH_3(H)SiCl_2$[f]	7.93	7.9 (3.65)[g]	1.64 (0.60)	0.50 (0.16)	5.5	240	375	N.D.[i]	—	—
$(CH_3)_2SiCl_2$	5.06	4.4	1.43	0.36	4.1	300	560	2.2	485	630
$(C_2H_5)_2SiCl_2$	1.87	0.4	0.10	0.05	N.D.	—	—	N.D.	—	—
$(CH_3)_2SiCl_2$ + CH_3SiCl_3 (3:1 molar ratio)	7.20	6.3	1.73	0.41	4.8	275	610	2.9	510	640
SE30		9.6[h]	2.99	0.78	9.6	325	615	9.5	285	615

a Polymer load before extraction, calculated from C, H analyses and extraction losses.
b Polymer load after extraction, calculated from C, H analyses.
c Middle (≈ inflection point) of final S-shaped decomposition curve.
e The last digit is not significant, but was included to precisely yield the extraction loss, when the "actual load" is subtracted from the "initial load".

d Extracted, non-heat treated phases.
e Data in parentheses are measured after the heat treatment.
f Calculated for $(CH_3SiO_{3/2})$ (see text).
g Calculated for $(CH_3SiO_{3/2})$ (see text).
h Not-extracted, of course.
i N D. = none detectable.

The chlorosiloxanes could then be used in a 30-h 100° fluidized bed polymerization. Rather than to optimize the process conditions for each monomer, the same conditions were used for all of them. This was done to provide a basis for comparing the resulting materials and predict the characteristics of products from various monomer mixtures. One such mixture, DMCS + MTCS in a 3:1 molar ratio, was included in this study.

Polymer load

The quantity of polymer coated on, and bonded to, the solid support was judged by exhaustive extraction, thermogravimetric analysis (TGA) in vacuum and C, H analysis. The results summarized in Table III show that only negligible amounts of the polymer could be extracted in most cases. These exhaustive extractions with benzene, conducted for 16 h in a Goldfisch apparatus, are roughly equivalent to soxhlet extractions four times as long. Under these conditions, limiting values of extractable material are reached[12].

The TGA and especially the C, H analysis showed that losses did occur, presumably in the fluidized-bed reaction. These losses were of tolerable magnitude (within the exploratory framework of this study at least), except in the case of the diethyldichlorosilane-based material. Clearly, lower polymerization temperatures — and perhaps an optimization of the partial hydrolysis step — would tend to reduce these losses.

It is readily apparent from Table III that TGA yields only a rough approximation on the amount of polymer present. The values are lower than those derived from C, H analysis, indicating non-volatile residues. On the other hand, the only non-support-bonded phase investigated in this study proved completely volatile in TGA. (Whether this method is indeed capable of differentiating between coated and support-bonded phases, could be ascertained only through further comparisons.) In the polymer derived from MTCS, the 760° temperature limitation of the thermobalance did not permit to scan the full temperature range of decomposition (Fig. 7). Consequently, only 1.1 % from a 9.4 % load show up as volatile (Table III).

The values for "% actual load" in the same table represent the means of the weight % of polymer values calculated from the % carbon and % hydrogen content. In most cases, these values were similar. If the amount of C and H introduced by the initial treatment with MTCS is considered negligible, the C/H ratio should be the same as in the monomer. This was the case within the apparent experimental error in all cases except methyldichlorosilane. The C/H weight ratio for $(CH_3HSiO)_n$ is 3.0; for

$(CH_3\overset{|}{\underset{|}{Si}}-O-)_n$ 4.0. The experimental value was 3.28, indicating partial oxidation. After the heat treatments, this ratio was again measured. It had changed to 3.75, close to the trifunctional polymer derived from MTCS.

In the case of this and other monomers, the criterion for inclusion in this study was their high volatility and commercial availability rather than their anticipated chromatographic performance. Therefore, it was surprising that some phases, for instance the above mentioned $(CH_3HSiO)_n$, performed rather well in the chromatographic tests (Figs. 1, 3, and 4). It is interesting to note that the TGA of this heat-treated material showed no detectable weight loss (Table III, Fig. 7).

The polymer derived from DMCS, of course, possesses characteristics similar to
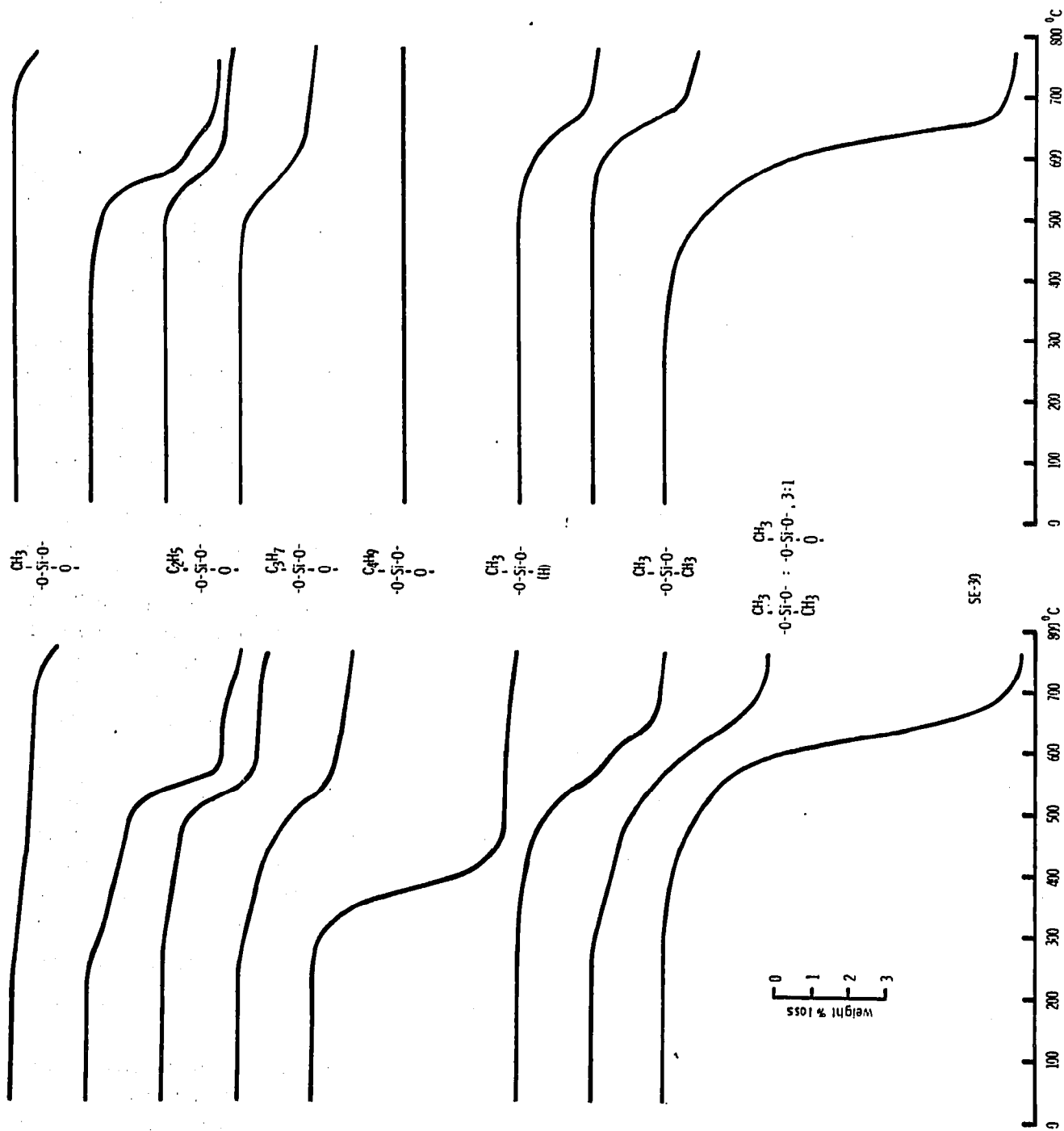
Fig. 7. TGA in vacuum of support-bonded liquid phases and SE-30. Formulas given concur with the left-hand side curves.

the dimethylpolysiloxane liquid phases rampant in the realm of GLC. One of these dimethylpolysiloxanes (General Electric's SE-30 GC-grade) was used as the standard phase for comparisons through various methods of testing. In the exhaustive extractions, for example, a load of 9.6 % SE-30 could be extracted, leaving a support which showed the same chromatographic behavior as uncoated Chromosorb G. (A small amount of SE-30 evidently stuck to the fluted flask used in the rotary evaporation coating technique and was thus lost to the phase, as shown by C, H analysis noted in Table III.)

In contrast, only a very small amount of the surface-bonded polymer derived from DMCS could be removed by extraction (Table III) and the remaining material showed typical GLC characteristics. Since DMCS would not be expected to yield a completely insoluble polymer, the conclusion is apparent that actual chemical bonding exists between the polymer and the solid surface.

The same reasoning does not necessarily apply to all of the phases synthesized in this study. One could imagine highly cross-linked, completely insoluble polymers being formed from trifunctional monomers, which would give the erroneous impression of complete surface-bonding in the exhaustive extraction tests. However, this seems improbable and we believe that the "% actual load" in Table III describes accurately the amount of surface-bonded polymer. This belief is supported by several earlier experiments, which involved polymers synthesized from trifunctional chlorosilanes in fluidized bed under similar conditions. These monomers, however, were coated on untreated supports and the resulting polymers proved largely or even completely extractable.

The various treatments and tests described under EXPERIMENTAL followed the same exact schedule for each one of the phases. They were designed to answer several questions: How well would a phase perform with various test compounds? Would its behavior change with successive heat treatments? Would it stand up to relatively high temperatures and how was the amount of bleed obtained in temperature programming going to be affected?

Heat-treatment

Commercial silicones are heat-treated (cured) after hydrolysis, resulting in the formation of chains from cyclic structures, an increase in molecular weight, cross-linking, etc. Surface-bonded phases, on the other hand, are "cured" *in situ operandi*, *i.e.*, in the chromatographic column during conditioning and ensuing operations.

Besides removing some of the volatile fractions of "regular" polymers, (as distinguished from support-bonded varieties), conditioning is believed to provide a more even coating of the support through local polymer flow or distillation. At the same time, silicones are subject to molecular rearrangements at higher temperatures. These rearrangements are the only obvious mechanism by which support-bonded phases can attain the slightly different coating characteristics which subsequently influence chromatographic performance. Curing can also be expected to change the diffusion coefficients of chromatographed substances and consequently their mass transfer resistance terms.

Column bleed and thermal decomposition

In this study, the method used to determine column bleed is a modified (and

abbreviated) version of the commonly employed one. Instead of selecting various temperatures and recording the column bleed at isothermal conditions at a steady state, we temperature-programmed the column and made bleed measurements in a "dynamic" state. This appears justified when several columns are compared at exactly alike conditions of carrier gas flow, program rate, etc. It gives a better picture of the column bleed to be expected in a temperature-programmed run than the steady state measurements. More important for us, however, this approach provided an exactly reproducible step (in terms of column history) in the succession of treatments and tests, and furthermore, greatly reduced time requirements.

Very little is known about the mechanism or the composition of GLC bleed from silicone liquid phases. The gas chromatographer is generally not too interested to know whether the bleed he experiences results from volatile fractions originally present in the silicone, or from thermal rearrangement resulting in volatile siloxanes, or from oxidative rupture of Si–C bonds by traces of oxygen in the carrier gas.

In this study, a hydrogen flame detector (FID) was used for its sensitivity and ruggedness. Since it essentially monitors combustible carbon, the amount of bleed measured is not exactly proportional to the loss of polymer incurred in comparing different phases. For example, the FID will respond stronger to bleed from $(C_4H_9SiO_{3/2})_n$ than from $(CH_3SiO_{3/2})_n$ on an equal weight basis. It is also known to respond in an irregular manner to silicon-containing compounds[20]. We have made no effort to correct for these effects, since the chemical composition of the bleed was not determined.

The bleed curves, plotted as usual in log A vs. $1/T$, are shown in Fig. 2. General Electric's SE-30 GC grade, a phase of low bleed, was included to allow comparisons. The three curves for each phase correspond to measurements after the 250°, 350°, and 400° heat treatments. We want to stress the point that such curves were not exactly reproducible. This was apparently due to the fact that several polymerization variables, and the heat treatments themselves, influenced the polymer structure and consequently the bleed behavior. This touch of irreproducibility is paralleled by the behavior of different batches of normal GLC phases, which any gas chromatographer can attest to.

The bleed curves in Fig. 2 generally show the expected reduction in bleed after heat treatments of increasing temperature. Where the 400° curve is higher than the 350° one, it appears likely that significant thermal rearrangement to more volatile fragments (decomposition) has occurred in the 400° heat treatment.

The polymer derived from MTCS behaves irregularly in bleed as well as in chromatographic characteristics. Its bleed curves, on the whole, are noticeably flatter than those of the other materials, indicating that chemical decomposition is less prevalent (as compared to volatilization). Indeed, the TGA curves of this material show that the final decomposition started at 680° and had not reached the inflection point of the S-curve at the temperature limit of the thermobalance. At this limit (760°), only a small fraction of the material had decomposed (Table III, Fig. 7). Therefore, the bleed plotted in Fig. 2 is obviously due to a small amount of volatile materials. While the surface-bonded polymer could be expected to be virtually devoid of bleed after suitable further conditioning, its chromatographic properties leave everything to be desired (Fig. 3). Viewed as an organic structure, however, its thermal stability is remarkable.

Some of the bleed curves apparently contain breaks. For instance, the materials conditioned at 250° show these breaks in a range between 220 and 260°; several of them show a break exactly at 250°. It may be interesting to speculate on the reasons for these breaks and their connection with conditioning and the above mentioned causes of column bleed. For purposes of comparison, we have included an angular scale of the slopes representing the apparent Arrhenius activation energies. Certainly the steeper parts of the curves are indicative of chemical reactions. We would like to stress, however, that our measurements were done in a dynamic system and are not directly amenable to the usual physicochemical treatment.

Furthermore, the different "actual loads" (Table III), and possible effects of silicone on the FID, render comparisons of different materials in regard to their bleed levels as semiquantitative at best. It has been our experience that support-bonded phases improve considerably more than regular phases with extended conditioning. Regular phases, of course, were heat-cured before reaching the consumer and are therefore less affected by such treatment. Since this study was directed toward the synthesis and comparison of polymers rather than their applications for the best possible chromatography, all polymers were treated alike. For optimal GLC, however, each phase should be conditioned according to its particular characteristics. It may be appropriate to note, furthermore, that chromatographic bleed curves *per se* may only tell part of the story and should be interpreted with due caution.

The amount of bleed, which can be expected from silicone liquid phases in GLC, is of great importance in several types of analysis, for instance in temperature-programmed trace analysis, in the use of certain detectors such as the Ni-63 electron capture detector, in the ever more popular gas chromatography–mass spectrometry combination, etc. Yet, there is but scant documented knowledge on this subject available and the choice of a column and its further treatment retain the flavor of an art.

In comparison with the GE-SE-30 GC-grade, which is noted for its thermal stability, the support-bonded phases showed bleed rates of comparable magnitude. $[(CH_3)_2SiO]_n$ was generally lower than SE-30. This is also evident for the TGA decomposition after the phases had been subjected to the various tests. The inflection points of the S-curves lie at 630° (support-bonded material) and 615° (SE-30). The C_1 to C_4 series of trifunctional compounds did not show any great differences in bleed. Thermal stability as measured by TGA half-life decreases with the increasing length of substituent hydrocarbon chains ($>760, 615, 555$, and 545; for C_1 through C_4). This decrease becomes small, however, as the chain length increases. Support-bonded $[C_{18}H_{37}SiO_{3/2}]_n$, for instance has a half-life temperature of 510° (ref. 21).

Cross-linking does not seem to reduce bleed (DMCS + MTCS *vs.* DMCS derived polymers) under the conditions of the experiment. Under the much harsher conditions of the much less sensitive TGA, however, the cross-linked polymer begins to show a small advantage. The middle ($\approx$ inflection point) of the S-curve lies at 630° for the difunctional polymer and at 640° for the mixed polymer. In comparison, this temperature for the trifunctional methyl polymer is higher than 760° (Fig. 7, Table III). The chromatographic efficiency of the purely difunctional $[(CH_3)_2SiO]_n$, however, is much better and this polymer would be the phase of choice for many applications.

No deliberate effort has been made to determine the life-expectancy of support-bonded columns. Judged from our limited experience in working with them for longer

periods of time, their life-expectancy should be comparable if not superior to regular GLC coatings of similar structure.

If comparisons between TGA in vacuum, and bleed experiments under nitrogen, are permissible, it would appear that the polymers up to 400° rearranged and lost some material, but did not lose their essential structure necessary for efficient GLC. On the contrary, GLC efficiency increased. This is borne out by the HETP values (Table II) and especially the analysis of test mixtures, which showed various degrees of improvement. Only one particular test (the analysis of alcohols on $RSiO_{3/2}$) showed some deterioration after the 400° heat treatment. From the viewpoints of both chromatography and polymer chemistry, the half-life temperatures found by TGA in vacuum are relatively high. In a nitrogen or helium environment, this stability would yet increase.

It is interesting to compare the TGA curves before and after the phases had gone through the various heat treatments. The final decomposition (the S-curve) remains similar, although shifting slightly to higher temperatures. There is present, however, a fraction which is lost at considerably lower temperatures. This fraction apparently accounted for most of the measured GLC bleed. A comparison of the two sides of Fig. 7 shows an all but complete disappearance of these less stable parts of the polymer caused by the heat treatments. Besides providing an instructive illustration to the effects of column conditioning, the TGA suggests that some further reduction in GLC bleed could still be achieved through additional conditioning.

A special case in thermal stability is $(CH_3HSiO)_n$. The polymer decomposes at the lowest temperatures of all the phases (Fig. 7, left side). Once it has gone through the heat-treatments, no weight loss is recorded anymore by TGA (Fig. 7, right side). The phase, however, showed reasonable GLC properties (Figs. 1 and 3). Therefore, a C, H analysis was again made and indicated a load of 3.65 %. This load was calculated as $(CH_3SiO_{3/2})_n$ because of its 3.75 C/H weight ratio. It should have shown up clearly in the TGA. Further studies to investigate the properties of the two most stable polymers, namely those derived from CH_3SiCl_3 and $CH_3(H)SiCl_2$, are under way.

Column efficiency

Fig. 3 shows the chromatograms of a mixture of even-numbered *n*-hydrocarbons. The best performing phases were $[(CH_3)_2SiO]_n$, (CH_3HSiO) and the propyl and butyl derivatives of the trifunctional series. $[(C_2H_5)_2SiO]_n$ effected a relatively poor resolution, possibly caused by its low load. $(CH_3SiO_{3/2})$ was the worst of all GLC phases; it is indeed questionable whether it still possessed properties of a liquid on the support. (The differences in height of the hydrocarbon peaks in the chromatograms are not significant; they resulted from different speeds of syringe withdrawal after injection by two operators.)

These hydrocarbon analyses illustrate GLC performance in terms of resolution, retention temperature and bleed. All variables such as carrier gas flow, column length, etc., were kept constant to permit comparison of different phases. In the ethyl–propyl–butyl series of trifunctional polymers, for instance, the resolution as well as the retention temperatures increase. This is obviously due to the increased interactions between the test compound hexadecane and the hydrocarbon substituents. The rise in baseline, as the final temperature of 350° is approached, visually demonstrates typical bleed levels.

In a mixture such as DMCS + MTCS, the trifunctional monomer serves to demonstrate the effects of cross-linking. Although the mixed polymer is still a satisfactory phase for some purposes, the HETP has risen from 0.10 cm for the pure $[(CH_3)_2SiO]_n$ to 0.21 cm through the addition of $CH_3SiO_{3/2}$ units (Table II). Trifunctionality is an apparent disadvantage in the lower members of the series (methyl, ethyl), but gives good results from propyl up. One of the best support-bonded phases ever synthesized $((n\text{-}C_{18}H_{37}SiO_{3/2})_n$, see ref. 12) is a member of this series.

The HETP measurements have been performed at the same conditions (especially the same carrier gas flow) for all columns. Consequently, they do not represent minima in the Van Deemter curve; although the chosen gas velocity was close to the optimum one for most columns (compare Fig. 5).

In these measurements, a pronounced dependence of the retention time of the test compound hexadecane on the structure and the thermal history of the column was noted. Fig. 8 gives a graphic presentation of retention times as related to prior heat treatments. The polymers derived from difunctional monomers showed no appreciable changes. Heat treatment of the trifunctional ones, however, caused marked increases in retention time. These polymers cause longer retention times even before heat treatment, apparently due to the length of their substituent hydrocarbon chains. It appears likely, although by no means proven, that further cross-linking is the predominant effect brought about by the rearrangement of silicones under thermal stress.

Methyl, propyl, and butyl form a consistent trifunctional series; ethyl deviates somewhat from the pattern. $(CH_3HSiO)_n$ does not conform to the pattern for difunctional polymers; this is in agreement with the conclusion, based on C, H analysis, that most of the Si–H bonds have been broken. The polymer would thus approach the characteristics of one derived from a trifunctional monomer.

Cross-linking, in this context, is a multi-faceted term. It could involve condensation of some residual silanol groups, rearrangements to higher molecular weight structures and/or the formation of three-dimensional networks.

It is interesting to note the increase in retention time and the decrease in HETP resulting from the heat treatments. Although the HETP depends on many factors, it can be assumed that the formation of a dense, three-dimensional network would have certainly increased the HETP considerably because of its effect on the diffusion coefficient of hexadecane in the stationary phase. Such was not the case. A closer examination of the problem alluded to would need to involve a better characterization of the liquid phases before and after heat treatments in terms of molecular weight, viscosity, etc. However, the presence of chemical bonding between the liquid phase and the support does not allow the use of some common analytical methods.

Where the extent of cross-linking is increased, the viscosity of the liquid phase increases and the diffusion coefficients decrease (for a detailed discussion of the subject, see ref. 22). Therefore, the slope of the Van Deemter plot at high flows $[8/\pi^2(1 - R)R \cdot d^2/D_1]$ can be used to estimate relative diffusion rates in comparing different phases at similar conditions.

The liquid film thickness d is roughly proportional to the weight % load and $(1 - R)R$ can be easily calculated from the chromatograms. Fig. 5 shows the Van Deemter plots of several support-bonded phases and SE-30. From this plot, relative diffusion rates can be obtained. If the standard phase SE-30 is arbitrarily assigned a value of 100, the diffusion rates for $(C_4H_9SiO_{3/2})_n$, $(C_2H_5SiO_{3/2})_n$, $[(CH_3)_2SiO]_n$ and
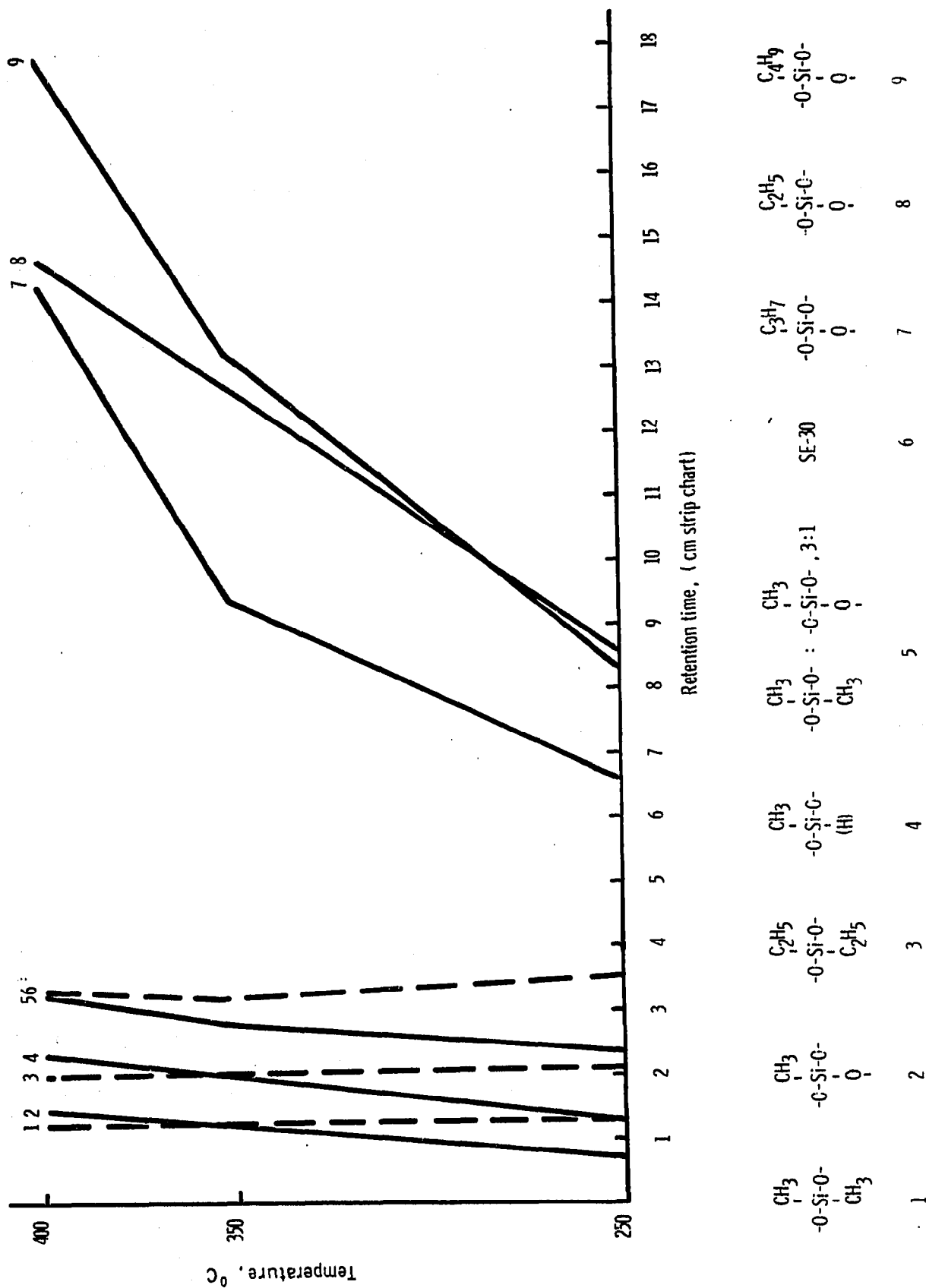
Fig. 8. Retention time of hexadecane as a function of heat treatments. Column, 0.50 m. × 4 mm I.D., glass. 190°; N$_2$ flow rate, 6.5 ml/min. Dotted line, difunctional polymers; full line, trifunctional polymers.

$[3(CH_3)_2SiO + CH_3SiO_{3/2}]n$ are 32.3, 8.3, 25.6, and 17.3, respectively. In this regard, SE-30 shows a distinctive advantage over all support-bonded phases including its counterpart $[(CH_3)_2SiO]_n$. Nothing is known about the "molecular weight" of the latter phase, nor about the extent of cross-linking caused by impurities, nor about the number of chemical bonds between liquid phase and Chromosorb surface. The last effect is, of course, peculiar to support-bonded phases. It should tend to increase the viscosity, decrease diffusion and raise the HETP.

Some or most of the characterized properties of support-bonded liquid phases from volatile monomers may well be similar to those of commercial silicones. A comparison with these products, however, is beyond the scope of this present study.

Chromatographic applications

The test mixtures, which were chromatographed after each heat treatment as described under EXPERIMENTAL, showed that adequate chromatography could be obtained from most phases. The performance (= separation and symmetry of peaks) improved somewhat with each heat treatment. The only exception found was the chromatography of n-alcohols (C_2 to C_{12}) which deteriorated on $(C_3H_7SiO_{3/2})_n$ and $(C_4H_9SiO_{3/2})_n$ after the 400° heat treatment. Fig. 1 shows a representative test mixture, Fig. 4 the above-mentioned alcohol mixture on three different phases. In the latter analysis, the change in retention time (temperature) was quite noticeable; this effect was strongly enhanced with the propyl and butylsilicones which caused extremely high retention temperatures of the alcohols. This provides yet another example for the contrast between di- and trifunctional polymers discussed above.

A number of applications appeared possible, of which we chose one related to other work in our laboratories. Several phases performed well with chlorinated hydrocarbon insecticides. Fig. 6 shows a sample chromatogram from a Ni-63 EC detector at high sensitivity. The amounts present, 1×10^{-12} g each of Lindane, Heptachlor, Aldrin and Heptachlorepoxide, and 2×10^{-12} g of Dieldrin, are close to the minimum detectable limits imposed by the detector (p,p'-DDT had been included, but failed to show up at these extremely low levels). The chromatogram indicates that support-bonded phases can be well used in trace analysis.

Some phases have also been successfully used in exploratory liquid–liquid chromatography; this study will be described in a later paper.

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