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# *IN SITU* SYNTHESIS OF SILICONE LIQUID PHASES FOR CHROMATOGRAPHY*

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## SUMMARY

Three typical silicone monomers have been coated on Chromosorb G and W supports and polymerized in gas chromatographic columns, using chemistry developed for support-bonded polymers. Fractional silicone losses occurred in the polymerization and heat-treatment steps, depending on monomer structure. The resulting materials were comparable to regular gas–liquid chromatographic phases; they also showed varying degrees of support-bonding.

## INTRODUCTION

In our previous reports[1,2] (see ref. 2 for pertinent literature), we have described two novel processes which produce polysiloxanes chemically bonded to the typical silicic surfaces of chromatographic supports. One process uses highly volatile silicone monomers, the other one monomers of low volatility. In both processes, the (final) polymerization takes place in a heated fluidized bed. This polymerization is a time-consuming step which requires suitable apparatus and is not easy to control. Consequently, further development in this area was sure to involve the conditions for polymerization since they determine, in large measure, success or failure in achieving support-bonding as well as the desired chromatographic performance.

When this paper was in its final experimental stages, MAJORS AND HOPPER[3] presented an excellent study which provides a case-in-point. They used the basic multi-step approach described in ref. 1, but conducted the critical polymerization in

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solution rather than in a fluidized bed. Their study is also remarkably complete: each of the synthetic steps was followed by IR spectral analysis, the support-bonded silicones were subsequently modified (by addition of polar substituents to vinyl groups), and the resulting materials performed well in liquid chromatography.

We had initially chosen the fluidized bed polymerization for theoretical reasons, yet had never established its particular characteristics as compared to other types of polymerization. This study, therefore, presents the same chemical approach toward the synthesis of chromatographic phases, but uses a polymerization technique other than the fluidized bed.

Of some consideration in the choice of this technique was the "typical" chromatographic laboratory, which appeared to be interested in using, but not in synthesizing, a particular type of silicone, especially when the procedure called for other than readily available laboratory apparatus. Perhaps the easiest route to silicones polymerized on adsorbent particles is to fill a chromatographic column with monomer-coated support, then saturate a suitable gas with water and blow it through the column until polymerization is complete. The feasibility of such a simplified "*in situ*" approach is investigated in this study. It should perhaps be mentioned that the idea to form chromatographic phases *in situ* is certainly not new and can be found in several variations in the literature[4–6]. To further favor a simplified approach, and to weigh against the quality of chromatography, only commercially available monomers were used; and they were used "as-received".

Thus, the basic approach was to polymerize, in the chromatographic column itself, silicone monomers coated on suitable supports, and to establish the performance of the resulting columns in gas–liquid chromatography (GLC). A variation of this procedure, designed to produce greater amounts of such phases, was to replace the chromatographic column by a suitably larger tube.

We also included two other variations in this study; first, a heat-treatment of the monomer-coated support in vacuum; and second, a heat-treatment of the polymerized phases in a nitrogen stream.

The first treatment was designed to point out possible effects resulting from a preferential coating of the outside of the porous Chromosorb with the monomer. Scanning electron microscopy of support-bonded phases polymerized in fluidized bed had shown the polymer to frequent predominantly the peripheral regions of the support particles[7].

The second treatment was intended to simulate gas chromatography (GC) column-conditioning and/or heat-curing of silicones, in order to point out any difference these treatments would engender in terms of chromatographic behavior or polymer structure. It should be noted, however, that this particular approach, *i.e.* heat-treatment in a nitrogen stream, was selected because it could be expected to define possible polymer losses and should closely resemble regular GC procedures. In contradistinction, the generally preferable method for heat-curing our types of silicone phases utilizes a closed vial under vacuum. This latter treatment avoids losses and increases, sometimes to a considerable extent, the percentage of support-bonded polymer.

Testing of the produced materials was to include general chromatographic performance [height equivalent to a theoretical plate (HETP), test mixtures], amount of surface-bonding [exhaustive extraction), and structure and molecular size distribu-

tion of extractable polymer (IR spectral analysis and gel permeation chromatography (GPC)[8]).

Our objectives were to show the feasibility of such a simplified approach with three model systems, and to characterize the resulting polymers to some extent. The choice of the three model systems reflects three major considerations. First, non-volatile monomers[1] *vs.* volatile monomers[2]; *viz.* $C_{18}H_{37}SiCl_3$ *vs.* $(CH_3)_2SiCl_2$, with $C_6H_5(CH_3)SiCl_2$ being processed both ways. Second, "hard-to-process" *vs.* "easy-to-process" monomers (as judged from the fluidized bed polymerization); *viz.* $C_6H_5(CH_3)SiCl_2$ *vs.* $C_{18}H_{37}SiCl_3$, with $(CH_3)_2SiCl_2$ occupying a medium position. Third, the formal similarity of some phases to commercial available ones; *viz.* $[(CH_3)_2SiO]_n$ to DC-200, SE-30, OV-1, OV-101; $[C_6H_5(CH_3)SiO]_n$ to OV-17, etc.

The following series of experiments is designed with the primary objective of defining differences between various approaches and materials, rather than obtaining the best performing phase from each monomer. A scheme of these experiments is shown in Fig. 1.

## EXPERIMENTAL

### *Treatment of the solid supports*

About 450 g of Chromosorb G, 100–120 mesh, "non-acid washed", (Johns-

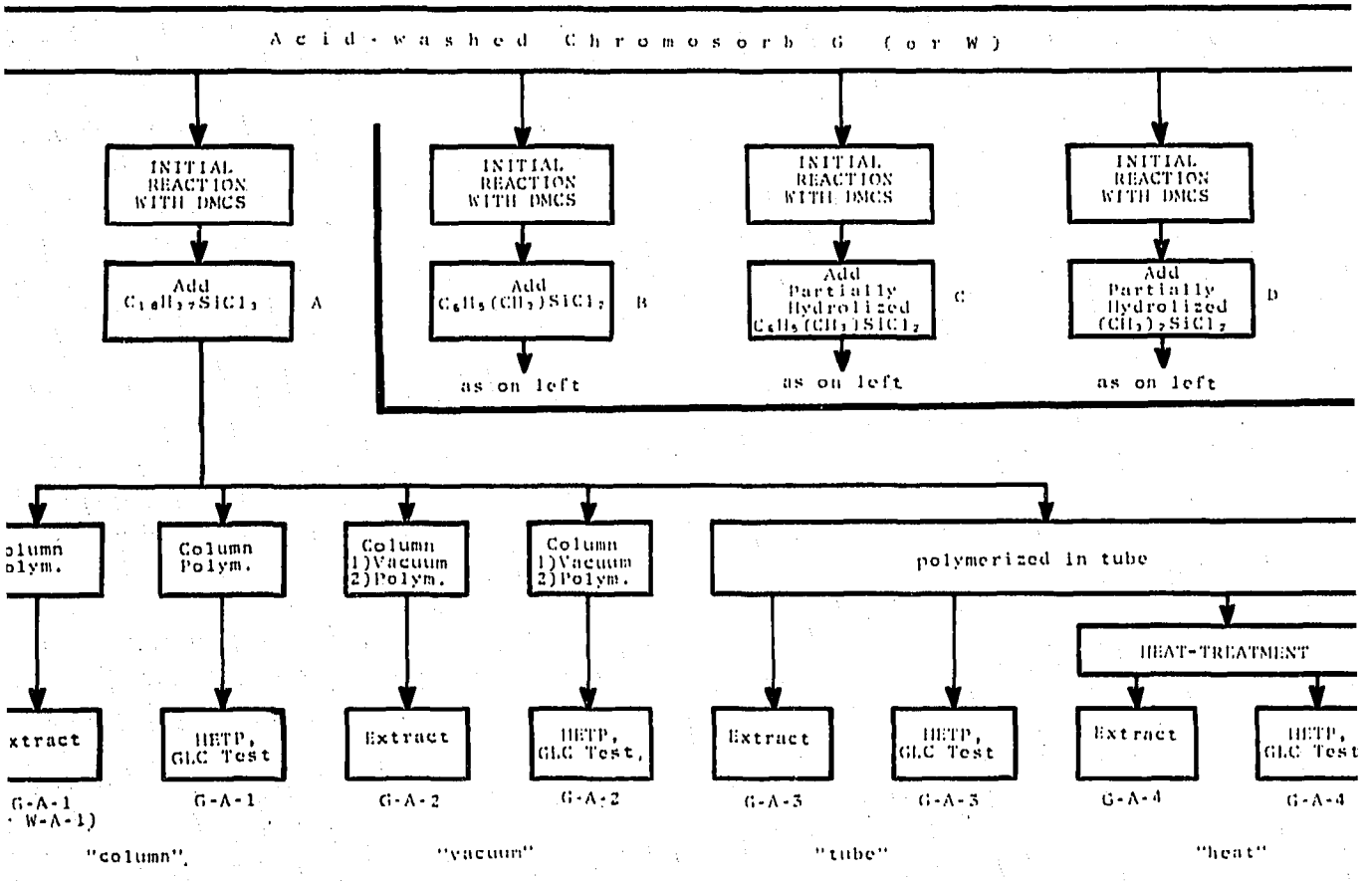


Fig. 1. Experimental scheme.

Manville) are covered with concentrated HCl and gently refluxed for 24 h, changing the HCl once at approximately 12 h. The Chromosorb is then washed with distilled water to neutrality; after decanting, most residual water is removed by several rinses with anhydrous acetone followed by drying in vacuum at 65°. The same procedure is used for 250 g of Chromosorb W, 100–120 mesh, "non-acid washed".

For the "initial reactions"[1], 100.00 g of the acid-washed Chromosorb G (50.00 g of Chromosorb W) are poured into 40 ml of dimethyldichlorosilane (DMCS) in enough toluene to cover the Chromosorb. The mixture is refluxed overnight (although 4 h would be considered sufficient). The excess DMCS and the toluene are removed by rotary evaporation at 65°.

*Treatment of the monomers*

The amount of monomer used is calculated to give a polysiloxane load of 5% for Chromosorb G and of 10% for Chromosorb W; defining percent load as 100 times the weight of the polymer divided by the weight of the Chromosorb + polymer.

Octadecyltrichlorosilane is treated as a non-volatile monomer[1], dimethyldichlorosilane is treated as a volatile monomer[2], and phenylmethyldichlorosilane is treated both ways. All three monomers had been purchased from Aldrich Chemical Company, Milwaukee, Wisc., U.S.A.

The volatile monomers are partially hydrolyzed[2] prior to coating on to the solid support as follows: To a magnetically stirred solution of the chlorosilane in 50 ml of acetonitrile, the solution of water in 30 ml of acetonitrile is added dropwise at room temperature. Four molar equivalents of chlorosilane are used for three molar equivalents of water. To preserve this ratio, the acetonitrile is dried before use and the partial hydrolysis is carried out under exclusion of atmospheric moisture. After the addition of chlorosilane is completed, more acetonitrile is added (enough to cover the Chromosorb to be added later) and the solution allowed to stand for 30 min.

The Chromosorb is then added to the acetonitrile solution of the monomer or partially hydrolyzed monomer. The acetonitrile is removed by careful evaporation in vacuum at 65°, leaving the dried material ready for polymerization.

*Polymerization*

The various batches of Chromosorb coated with the monomers or partially hydrolyzed monomers are used in the following manner:

(1) Two GLC glass columns (Microtek MT-220, 80 cm × 4 mm I.D.) are filled with the coated support. One column is packed in a similar manner to regular columns for GC. The other one is packed with only 3 g of the coated Chromosorb, destined to be exhaustively extracted subsequent to polymerization.

(2) Two GLC glass columns are filled with each of the phases as above. One end of each column is closed, and a vacuum of approximately $10^{-2}$ Torr applied. The column is sealed under vacuum and heat-treated for 45 min at 200° for $C_{18}H_{37}SiCl_3$, 100° for $C_6H_5(CH_3)SiCl_2$, and 150° for pre-polymerized $(CH_3)_2SiCl_2$. It is then cooled slowly to room temperature before breaking the seal.

The four GLC columns from above (C-1 and C-2) are connected to a multiplexer with suitable valves, and water-saturated $N_2$ is passed through at room temperature at a rate of 0.5–1 ml/min per gram of Chromosorb.

(3) The rest of the coated Chromosorb is placed in a U-shaped glass tube,

50 × 2.8 cm I.D., and is polymerized at room temperature with water-saturated air or nitrogen at approximately 0.5–1 ml/min per gram of Chromosorb.

Most polymerizations are complete within 20 h as indicated by the absence of HCl in the effluent gas.

*Heat-treatment*

The bulk of the material polymerized in the U-tube (C-3 above) is divided. One part is used directly for testing, while the other part is first heat-treated at 300° and then tested. The heat-treatment is performed in a *ca.* 36 × 2.5 cm I.D. Pyrex tube placed in a tubular furnace, under a slow flow of dry nitrogen. The temperature is monitored on a strip chart recorder; a typical profile is shown in Fig. 2.

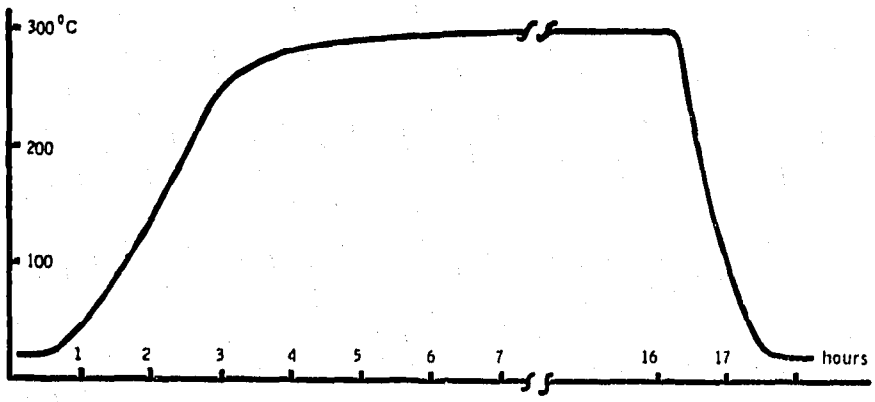


Fig. 2. Temperature profile of heat-treatment.

*Characterization of chromatographic phases*

*Extraction.* About 3 g of each of the polymerized materials (including heat-treated ones) were extracted exhaustively in a Goldfish (Extractor Fisher Scientific Co., St. Louis, Mo., U.S.A.) with benzene for 16 h. Table I indicates the extractable amounts as the difference between columns 3 and 4, the "*Polymer loads (%) Before*" and "*After extraction*". Some of the extracted polymers were analyzed by GPC to obtain their molecular size distribution.

*Column efficiency and performance.* Unextracted chromatographic materials, of both the heat-treated and non-heat-treated varieties, were used to pack 80 cm × 4 mm I.D. glass columns. These Microtek columns (together with those used from a polymerization *in situ*, see C-1 and C-2 above) were conditioned for 2 h at 100°, followed by 2 h at 150° and 16 h at 250°, at a $N_2$ flow rate of 15–20 ml/min. These columns were to be used to: (a) chromatograph a 1% solution of hexadecane in pentane at 152° and a $N_2$ flow rate of 33 ml/min to determine the HETP at a common $N_2$ flow rate. Note that these values are not HETP minima. Table I lists the partition ratio $k$ for hexadecane. For calculation of the latter values, the 12–14-sec time intervals between injection and appearance of the solvent pentane, which is assumed to be unretarded, were measured with a stopwatch for accuracy. HETP and $k$ values represent averages from at least three injections; (b) chromatograph a mixture containing polar compounds such as acids, phenols and alcohols.

TABLE I

| *Monomer* | *No.* | *Process* | *Polymer load (%)*[c] | | *HETP (mm)*[c] | *k (average)*[c] | *Chromatography of polar compounds* |
|---|---|---|---|---|---|---|---|
| | | | *Before extraction*[a] | *After extraction*[b] | | | |
| $C_{18}H_{37}SiCl_3$ | G-A-1 | Column | | | 0.66[d] | 11.8[d] | Good |
| | 2 | Vacuum | | | 0.62[d] | 13.1[d] | Good–bleeds slightly |
| | 3 | Tube | 5.66 | 3.97 | 0.59[d] | 12.9[d] | Good |
| | 4 | Heat | 5.52 | 4.67 | 0.77[d] | 13.0[d] | Good |
| $C_6H_5(CH_3)SiCl_2$ | G-B-1 | Column | | | 1.64 | 34.5 | Fair/poor |
| | 2 | Vacuum | | | 0.57 | 33.6 | Good |
| | 3 | Tube | 4.68 | −0.49 | 0.42 | 43.3 | Good |
| | 4 | Heat | 3.55 | 2.99 | 0.41 | 35.6 | Good |
| $C_6H_5(CH_3)SiCl_2$, pre-polymerized | G-C-1 | Column | | | 0.73 | 13.5 | Very good |
| | 2 | Vacuum | | | 0.80 | 27.0 | Good |
| | 3 | Tube | 4.26 | 0 | 0.78 | 11.5 | Good |
| | 4 | Heat | 1.10 | 0.39 | 0.79 | 13.4 | Good |
| $(CH_3)_2SiCl_2$, pre-polymerized | G-D-1 | Column | | | 0.59 | 21.7 | Good/very good |
| | 2 | Vacuum | | | 1.17 | 26.3 | Good/fair |
| | 3 | Tube | 2.13 | 0.29 | 0.48 | 21.3 | Good |
| | 4 | Heat | 1.70 | 0.30 | 0.50 | 20.5 | Good |
| $C_{18}H_{37}SiCl_3$ | W-A-1 | Column | | | 0.65[d] | 9.9[d] | Good |
| | 2 | Vacuum | | | 0.63[d] | 10.6[d] | Good |
| | 3 | Tube | 10.02 | 8.16 | 0.82[d] | 10.4[d] | Good |
| | 4 | Heat | 9.80 | 7.70 | 0.64[d] | 10.3[d] | Good |
| $C_6H_5(CH_3)SiCl_2$ | W-B-1 | Column | | | 0.70 | 17.3 | Good |
| | 2 | Vacuum | | | 0.62 | 16.6 | Good |
| | 3 | Tube | 8.69 | −0.09 | 0.60 | 17.8 | Good |
| | 4 | Heat | 6.20 | 5.04 | 0.52 | 18.5 | Good |
| $C_6H_5(CH_3)SiCl_2$, pre-polymerized | W-C-1 | Column | | | 0.61 | 8.7 | Good/very good |
| | 2 | Vacuum | | | 0.69 | 26.6 | Fair–bleeds badly |
| | 3 | Tube | 10.77 | 0.07 | 0.58 | 9.0 | Good |
| | 4 | Heat | 2.53 | 1.60 | 0.77 | 8.9 | Good |
| $(CH_3)_2SiCl_2$, pre-polymerized | W-D-1 | Column | | | 1.08 | 6.6 | Poor–bleeds |
| | 2 | Vacuum | | | 4.47 | 7.3 | Very poor–bleeds |
| | 3 | Tube | 1.82 | −0.06 | 0.59 | 6.0 | Poor–bleeds |
| | 4 | Heat | 1.36 | 0.48 | 0.87 | 7.0 | Poor–bleeds |

[a] Polymer load before extraction, calculated from C analysis.
[b] Polymer load after extraction, calculated from [a] less the amount of extractable polymer.
[c] All HETP values are measured on non-extracted materials using 1% hexadecane in pentane at *ca.* 33 ml/min, $N_2$ and 152° except where indicated by [d].
[d] Same as [c] but measured at 215°.
[e] Theoretical = 5.0% (G) or 10.0% (W).

*Molecular weight distribution profiles by gel permeation chromatography*. Some of the polymers extracted by benzene were analyzed for molecular weight distribution (MWD) using a Waters Associates Inc. Model 200 Gel Permeation Chromatograph equipped with a set of four Styragel columns with nominal exclusion porosities of $10^6$, $10^5$, $10^4$ and $10^3$ Å. The chromatograph is operated at ambient temperature,

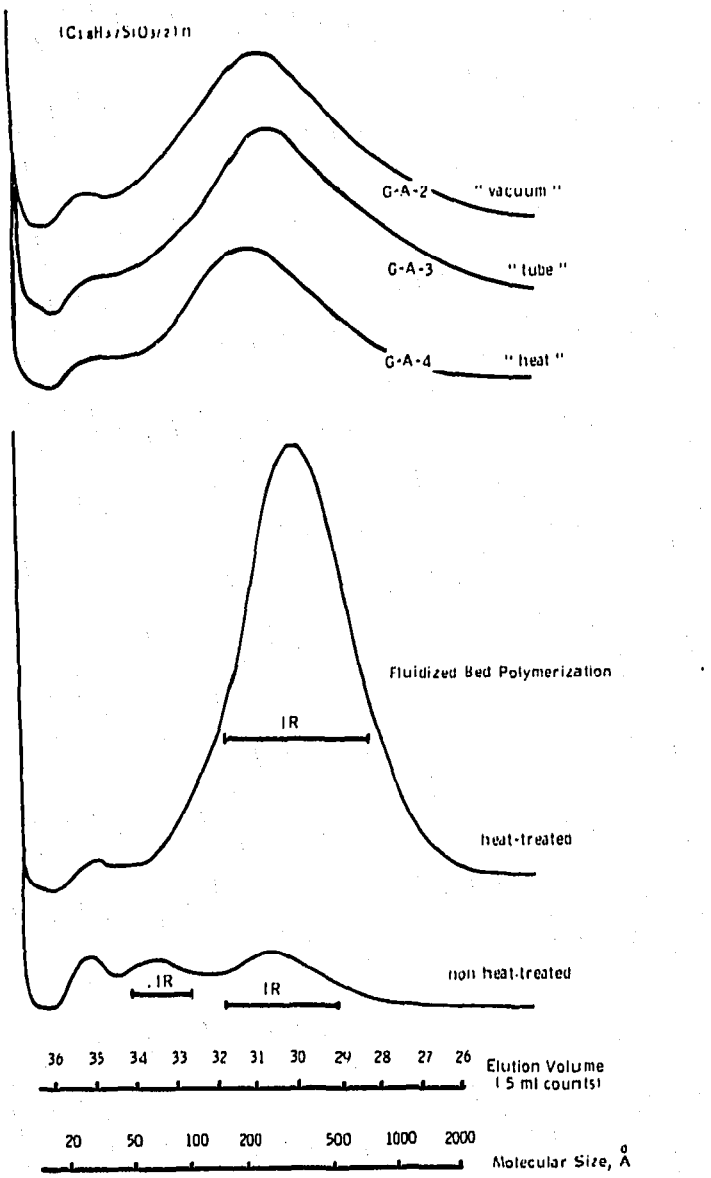


Fig. 3. Molecular weight distribution of polyoctadecylsiloxane from *in situ* and fluidized bed polymerizations.

a 1 ml/min tetrahydrofuran (THF) flow, and an injection time of 120 sec. A differential refractometer serves as detector, whose signal amplification is adjusted to accommodate the large difference in response between the dimethylsiloxanes and the phenylmethylsiloxanes, as well as different amounts of polymer. Consequently, the various gel permeation chromatograms are comparable to each other only in terms of molecular size distribution (abscissa), but not in terms of signal amplitudes or polymer amounts (ordinate).

Excess solvent (benzene) was removed from the silicone extracts to give a volume of 1–4 ml, containing 15–60 mg of polymer. The samples were then diluted with THF to a final volume of 5 ml and a suitable amount, usually 5–10 mg of polymer, applied to the GPC column. This procedure was used because some samples

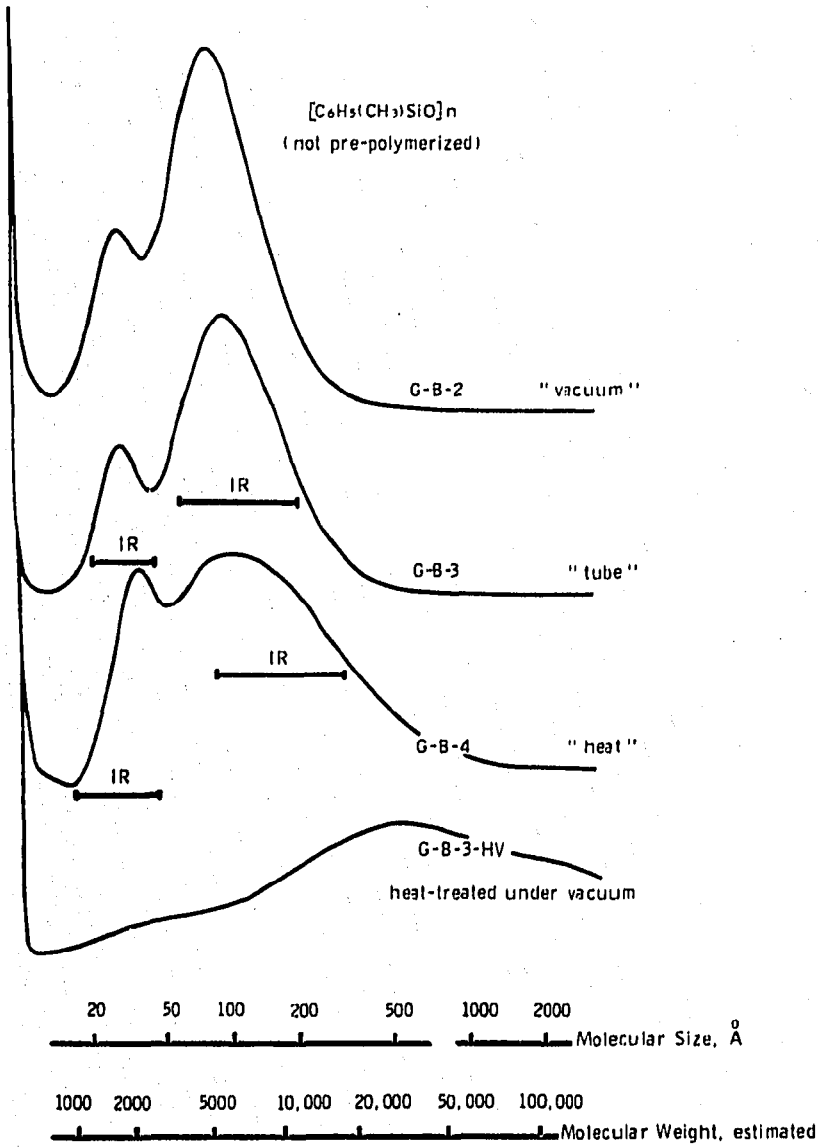


Fig. 4. Molecular weight distribution of non-pre-polymerized polyphenylmethylsiloxane.

could not be dissolved in the eluent THF, once benzene has been completely removed. The rising contour of the benzene peak concludes the GPC curves as seen in the left sides of Figs. 3–7; it does not interfere with the MWD analysis.

The Styragel column set had previously been calibrated with narrow-distribution polystyrene standards. The number and weight-average molecular sizes for the various silicone samples are calculated from manual peak height measurements and a computer program using the polystyrene calibration data. From previous characterization data on broad-distribution polydimethylsiloxane fluids, a conversion factor ($Q = 34$) was used to express the molecular size data of polydimethylsiloxanes in terms of molecular weight.

An analogous conversion factor is unknown for the other two polymers. Assuming the same straight-chain siloxane backbone for dimethyl- and phenylmethyl-

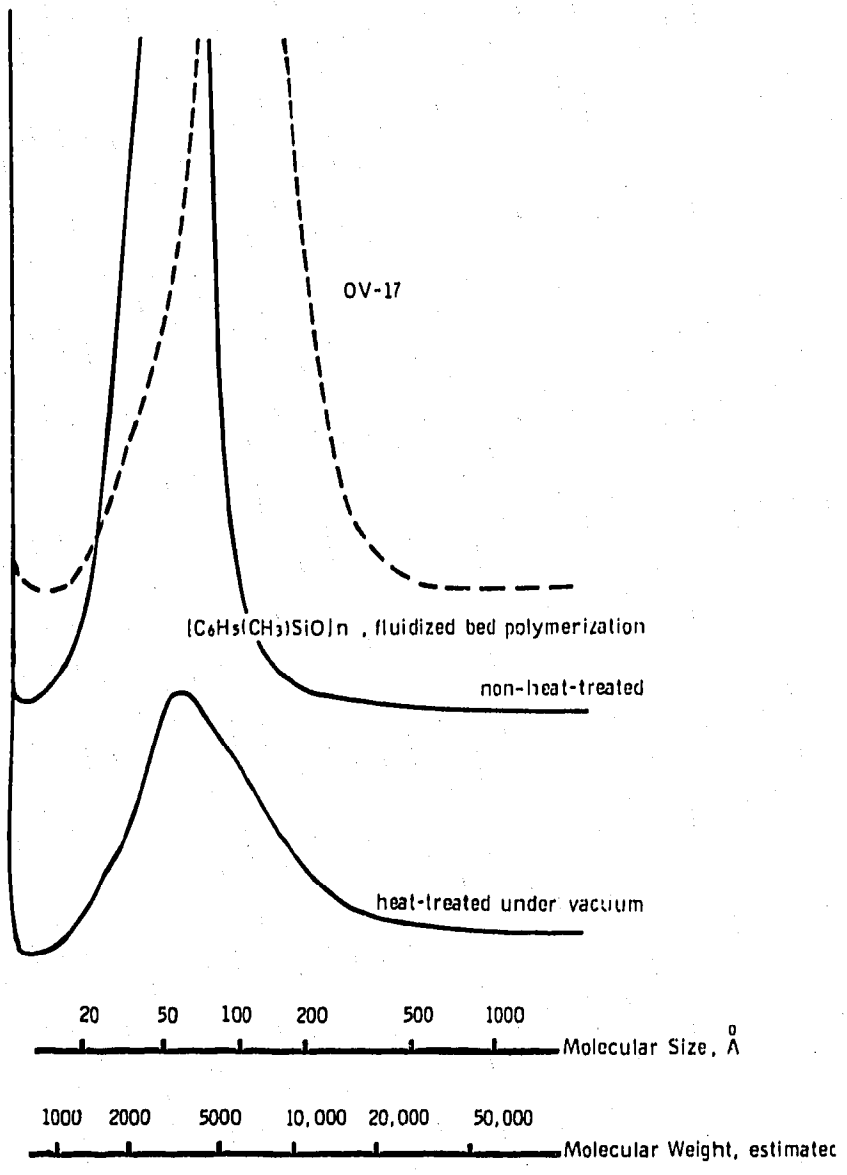


Fig. 5. Molecular weight distribution of fluidized bed polymerized polyphenylmethylsiloxane.

silicones, $Q$ values of 50–60 may be estimated for the latter. Molecular weight abscissae based on $Q = 54$ are therefore included in Figs. 4–6 for a rough orientation.

No such estimate appears justified for polyoctadecylsiloxane, especially since this polymer is possibly highly branched. The molecular size data for all three polymers appear in Table II, and the corresponding gel permeation chromatograms are shown in Figs. 3–7, including a commercial phase and some phases prepared by fluidized-bed polymerization, for purpose of comparison.

*Infrared analysis of polymer fractions.* Selected samples were rerun about five months after the initial GPC analysis to determine reproducibility and possible ageing effects as well as to obtain fractions for subsequent IR analysis. These materials were selected on the basis of their essentially bimodal molecular distribution and 5–15-ml eluent fractions were taken as indicated in the figures by the designation "IR". The eluent THF was evaporated under dry nitrogen and the IR spectra

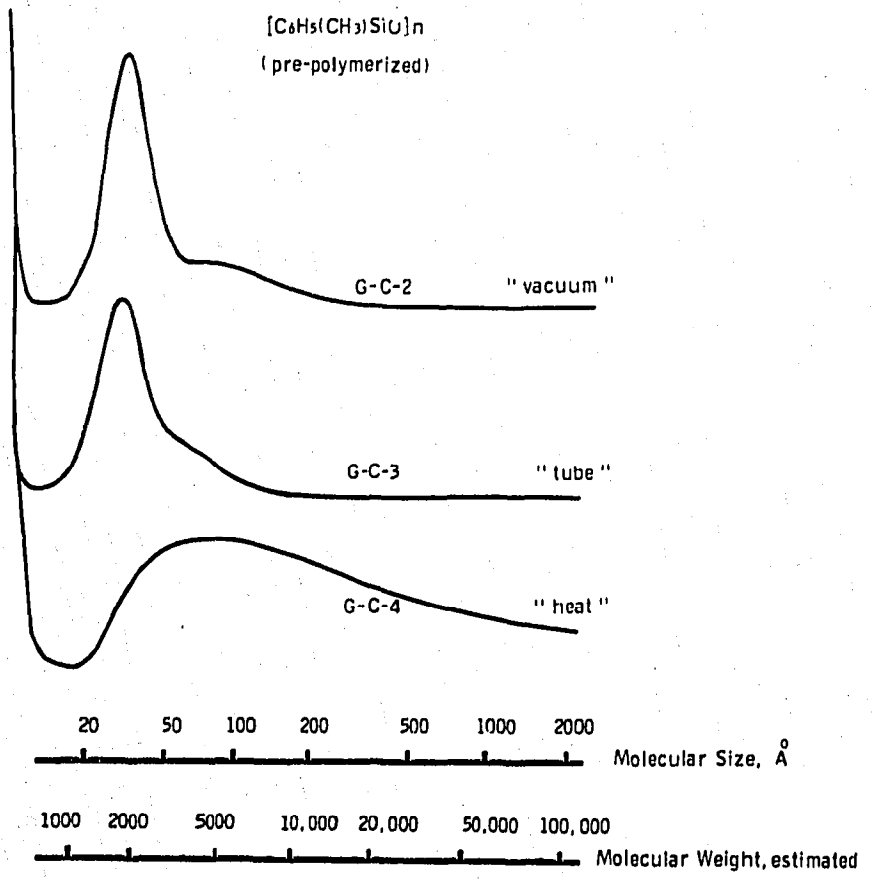


Fig. 6. Molecular weight distribution of pre-polymerized polyphenylmethylsiloxane.

obtained from methylene chloride-cast films using a Perkin-Elmer Model 221 IR spectrophotometer equipped with sodium chloride optics.

## RESULTS

### *Phase losses and support-bonded fractions*

Table I summarises the various measurements performed on the polymerized materials; the designations correspond to those introduced in the flow-chart (Fig. 1). The third column, "*Polymer load (%), Before extraction*", is derived from carbon combustion analysis. These values should reach a theoretical 5 and 10% for phases on Chromosorb G and W, respectively; with a small amount added as a contribution from the "initial reaction" with DMCS.

Low values in this category indicate losses of silicon compounds in the polymerization step (lines 3, "tube") and losses in the aggregated polymerization and heat-treatment steps (lines 4, "heat"). The polymers listed in lines 1, "column", and lines 2, "vacuum", have not been similarly analyzed; however, they are most likely to resemble those listed in lines 3.

Values in the next column, "*Polymer load (%), after extraction*", represent the difference between the above mentioned, original polymer loads and the amount of

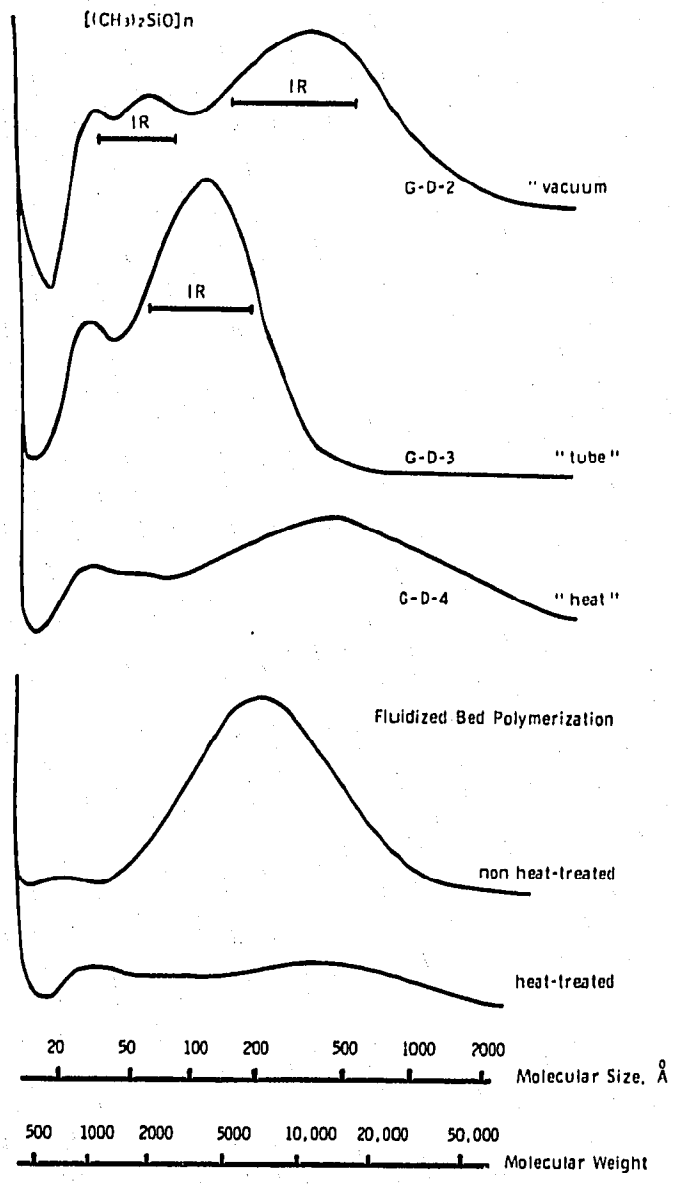


Fig. 7. Molecular weight distribution of polydimethylsiloxane.

extractable polymer. They indicate the amount of support-bonded polymer, a value which would be especially significant if such materials were destined to be used in liquid chromatography. Small negative values in this column are due to the contribution of the "initial reaction" to an extractable polymer.

From the data listed in these two columns, the following trends can be observed: virtually no losses occur from the octadecyl phase in polymerization and heat-treatment. The two phenylmethyl phases lose only negligible amounts in the polymerization, but the pre-polymerized one is decimated in the subsequent heat-treatment. This is most likely due to the predominance of a cyclic tetra- or penta-siloxane (Fig. 6). The dimethyl phase, which is the most volatile of the three materials, suffers severe losses during polymerization.

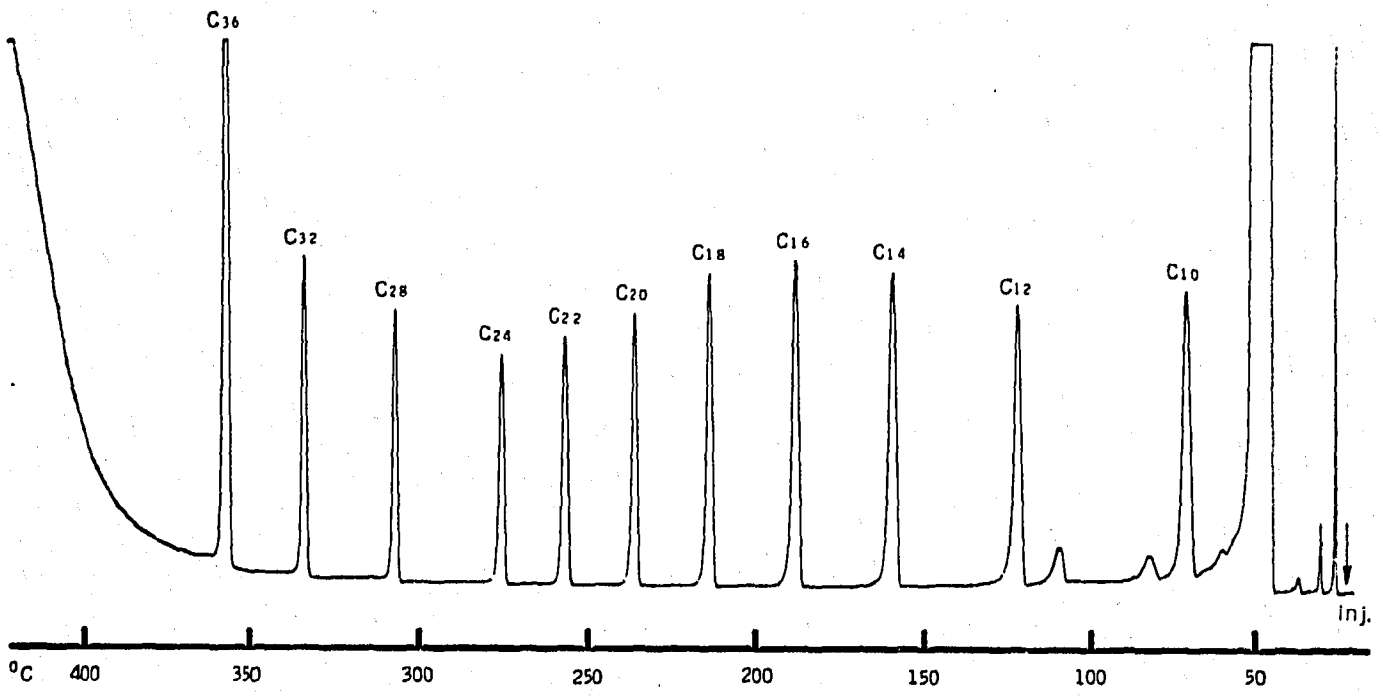


Fig. 8. Chromatogram of *n*-hydrocarbons. Column: *ca.* 5% by wt. polyoctadecylsiloxane on 100–120 mesh Chromosorb G, 0.5 m × 4 mm I.D. Pyrex glass (Perkin-Elmer 800, flame ionization detection). Initial temperature, 30°, programmed at 16°/ min up to 410°. $N_2$ flow rate, 13 ml/min. The injection mixture contained *ca.* 4 $\mu$g of each hydrocarbon except $C_{36}$.

Heat-treatment generally causes some polymer losses, a process which could be expected to occur in high-temperature GC conditioning, and could possibly have been averted in this synthetic procedure by curing in a closed system. As an additional effect, heat-treatment in most cases increases the relative amount of support-bonded polymer significantly.

*Gas chromatographic performance*

In general, the GC performance of most of the described phases is similar to that which one would expect of well-conditioned, corresponding commercial silicones coated on highly deactivated supports. Very little tailing is noticeable, and heat-treatment does not further improve GLC performance. The vacuum heat-treatment of the monomer-coated supports, on the other hand, proves definitely detrimental, possibly by causing the monomer to rearrange.

The polymerization *in situ*, in the GC column itself, seems to be slightly better than the other approaches in terms of peak tailing, but the advantage is not very pronounced. This effect may originate from some monomer transferring to the column wall, reacting with surface silanol groups and possibly polymerizing there.

With some exceptions, a good concurrence of results can be obtained from Chromosorb G and W; in chromatographic performance as well as in relative polymer loads.

Except as noted in Table I, column bleed is comparable to high-performance GLC phases. Fig. 8 shows the bleed from a single column GC, using a G-A-4 sample which had been previously conditioned at 400° for 1 h.

TABLE II

$\bar{A}_n$ = number-average molecular size; $\bar{A}_w$ = weight-average molecular size; $\bar{M}_n$ = number-average molecular weight; $\bar{M}_w$ = weight-average molecular weight.

| *Monomer* | *No.* | *Process* | *Fig. No.* | $\bar{A}_n$ | $\bar{M}_n$[a] | $\bar{A}_w$ | $\bar{M}_w$[a] |
|---|---|---|---|---|---|---|---|
| *In situ polymerization* | | | | | | | |
| $C_{18}H_{37}SiCl_3$ | G-A-2 | Vacuum | 3 | 149 | | 424 | |
| | G-A-3 | Tube | 3 | 164 | | 549 | |
| | G-A-4 | Heat | 3 | 131 | | 281 | |
| $C_6H_5(CH_3)SiCl_2$ | G-B-2 | Vacuum | 4 | 52 | 2,800 | 83 | 4,500 |
| | G-B-3 | Tube | 4 | 60 | 3,200 | 103 | 5,600 |
| | G-B-4 | Heat | 4 | 71 | 3,800 | 160 | 8,600 |
| $C_6H_5(CH_3)SiCl_2$ | G-C-2 | Vacuum | 6 | 31 | 1,700 | 43 | 2,300 |
| (pre-polymerized) | G-C-3 | Tube | 6 | 28 | 1,500 | 34 | 1,800 |
| | G-C-4 | Heat | 6 | 93 | 5,000 | 650 | 35,100 |
| $(CH_3)_2SiCl_2$ | G-D-2 | Vacuum | 7 | 108 | 3,700 | 343 | 11,700 |
| (pre-polymerized) | G-D-3 | Tube | 7 | 65 | 2,200 | 114 | 3,900 |
| | G-D-4 | Heat | 7 | 147 | 5,000 | 620 | 21,000 |
| *Fluidized bed polymerization* | | | | | | | |
| $C_{18}H_{37}SiCl_3$ | | Non-heat-treated | 3 | 68 | | 179 | |
| | | Heat-treated, $N_2$ | 3 | 223 | | 398 | |
| $C_6H_5(CH_3)SiCl_2$ | | Non-heat-treated | 5 | | | | |
| | | Heat treated under vacuum | 5 | 58 | 3,100 | 86 | 4,600 |
| $(CH_3)_2SiCl_2$ | | Non-heat-treated | 7 | 158 | 5,400 | 285 | 9,700 |
| | | Heat-treated, $N_2$ | 7 | 95 | 3,200 | 342 | 11,600 |

[a] Molecular weights for polyphenylmethylsiloxanes are estimated by using a factor $Q=54$ for converting molecular size to molecular weight data.

*Polymer structure*

*Polyoctadecylsiloxane.* Fig. 3 shows the molecular size distribution of the extractable polymer fractions, both from *in situ* and fluidized bed polymerizations. The elution volume of the main peak corresponds to that of a linear hydrocarbon molecular weight of 3,000–4,000; the actual molecular weight of the trifunctional silicone is in all likelihood considerably higher. The IR spectra of this main fraction are consistent with a (probably highly branched) polyoctadecylsiloxane.

Omitted in Fig. 3 is a small fraction of high molecular weight (>1,000,000, as judged from a molecular size of about 500,000 Å) which shows up in the heat-treated material obtained by fluidized bed polymerization. Its IR spectrum shows only methylene and the 720 wavenumber absorption due to $-CH_2-$ rocking in long alkane chains, as well as some atypical siloxane absorption at 1000–1100 wavenumbers. No particular structure could be assigned.

In contrast, the small peak of low molecular weight has an elution volume and IR spectrum almost identical to that of the low molecular weight fraction of the vacuum-treated dimethyl phase. It is a polydimethylsiloxane with an average molecular weight of 1,800 and owes its existence quite apparently to the DMCS employed in the "initial reaction".

*Polyphenylmethylsiloxane.* The molecular size distribution of these phases is shown in Figs. 4 and 6. The directly polymerized phase (no prepolymerization in solution) has a bimodal profile (Fig. 4). The smaller peak of lower molecular weight represents most probably a tetra- or penta-cyclic phenylmethylsiloxane. The IR spectrum includes a strong peak at 1080 wavenumbers indicative of a cyclic siloxane; hydroxyl absorption is completely absent.

The main peaks of G-B-3 and -4 appear in approximately the same molecular weight range as OV-17, a commercially available polyphenylmethylsiloxane. Their IR spectra are almost identical to that of OV-17. One noticeable difference is the presence of hydroxyl groups in G-B-3 which are absent or at least greatly reduced in the heat-treated material G-B-4. The heat-treatment thus apparently furthers the condensation of silanol groups, as could be expected.

Included in Fig. 4 is a modified G-B-3 material, designated G-B-3-HV. This phase had been polymerized in a tube as described earlier, but was then dried in vacuum at 100°, and heat-treated in a vial (closed under high vacuum) at 300° for 18 h.

A phase polymerized in a fluidized bed was afforded a similar heat-treatment in vacuum. Fig. 5 shows that this polymerization, in contrast to the above, did not appreciably change the apparent molecular weight distribution. It did, however, decrease the fraction of extractable polymer. Incidentally, a similar heated phase showed excellent GLC performance, especially with highly polar compounds such as the N-trifluoroacetyl-*n*-butyl ester derivatives of amino acids[9].

*Polyphenylmethylsiloxane, pre-polymerized.* The pre-polymerized phenylmethylsiloxane shown in Fig. 6 possesses a MWD significantly different from that of the directly polymerized phase described above. The cyclic siloxane is predominant, causing the severe losses of phase in the heat-treatment under a nitrogen stream (Table I, W-C-4 and G-C-4 as compared to W-C-3 and G-C-3). A small fraction of the cyclic material rearranges to an assumedly linear polymer of higher molecular weight, as indicated by the IR spectra of the total extractable material (= material not fractionated by GPC).

*Polydimethylsiloxane.* This phase is shown in Fig. 7; a variety of distribution profiles can be observed. Heat-treatment broadens the MWD, both for fluidized bed and *in situ* polymerized phases, an effect which is not necessarily desirable.

All IR spectra are consistent with linear polydimethylsiloxanes. The higher molecular weight fractions (4,000 for G-D-3 and 12,000 for G-D-2) are identical. The lower molecular weight peaks, 700 (or 8 dimethylsiloxane groups) for G-D-3 and 1,800 (25 such groups) for G-D-2,show significant amounts of trimethylsiloxy terminal groups in their IR spectra. These groups most likely originated from small amounts of trimethylchlorosilane present in the commercially available DMCS.

No ageing effects were noticed by GPC (five months after the initial analysis) for any of the three types of polymer.

## DISCUSSION

In this study, we have used the chemistry developed in our earlier attempts to produce support-bonded silicones[1,2]. However, our primary objective was to demonstrate the feasibility of polymerizing silicones on supports in a simple manner,

regardless of whether the resulting materials turned out to be support-bonded or not. It appears that only small additional benefits can be reaped from the presence of support-bonding in pure silicones when used for GC (as opposed to, say, liquid chromatography); but the possibility to produce, in this manner, types of silicone liquid phases which cannot be commercially obtained may prove worthy of some consideration.

It appeared certain from the onset of this study that it should be possible to polymerize silicones by passing water-saturated gas through monomer-coated supports. The significant point, however, was whether the resulting materials would prove fit for chromatographic service. After all, considerable problems and critical precautions can be associated with even the regular coating techniques for difficult types of analysis. This fact underlines the importance of evenly distributed polymer layers for good chromatographic performance.

In contrast to the polymerization in a fluidized bed[1,2] polymerization *in situ* occurs on particles fixed in a specific position. Furthermore, the direction of flow of water-saturated gas establishes conditions for polymerization (notably the concentrations of $H_2O$ and HCl in the gas), which vary along different longitudinal positions in the column, and the influence of varying local flow through channels due to clusters or striae of support particles is also involved.

Not only could the evenness of coating be questioned, but there was also to be considered the nature of the synthesized polymers, *i.e.* their molecular weight distribution, residual silanol groups, etc. It was with these questions in mind that the HETP and $k$ measurements as well as the GPC and the subsequent IR studies were conducted. The HETP values are influenced by the evenness of otherwise similar polymer layers, while the $k$ values, at comparable loads, should indicate any gross structural change in the polymer. The latter case, for instance, may have occurred with the G-C-2 and W-C-2 phases (Table I) in the vacuum heat-treatment.

From a GC viewpoint, the three model phases generally performed well. They were definitely comparable to the performance expected of corresponding conventional materials. Heat-treatment increased the average molecular weight and the amount of support-bonding; it did not change significantly general GLC performance. One should expect, though, that the resulting reduction in silanol groups could make the difference in critical types of analysis.

The conditions of heat-treatment (300° under a flow of nitrogen) were definitely too harsh for the phenylmethyl and dimethyl phases and resulted in severe silicone losses. In these cases, heat-treatment in a closed system (or the conventional "no-flow conditioning") should be preferable. Fig. 4, for instance, includes for comparison a phenylmethyl phase thus treated.

From a synthetic viewpoint, the volatility of the monomer (and of polymer fractions of low molecular weight) plays a significant role. Exactly the same conditions were, of course, used in the polymerization of all three monomers, and apparently they suited octadecyltrichlorosilane well but caused severe losses of the more volatile materials. A practical application of the described procedures for the phenylmethyl and especially the dimethyl phases would therefore require their prior modification.

Several other considerations emerged from this study; obvious ones, perhaps, yet easy to overlook. First, the correlation between the MWD of a polymer, and its

performance in chromatographic separations, is a generally neglected, yet quite interesting subject. Certainly silicones can be expected to change considerably in their MWD between the time when they are coated on to GLC supports and the time when the column is finally discarded. And it is obvious that, among other effects, the polymer's MWD can be expected to influence the solute diffusion rate and consequently the mass transfer resistance term in the Van Deemter equation.

GPC is the obvious method of choice for establishing the MWD of experimental polymers as they are formed in our experiments, but one point should be noted. In our special case, GPC is of necessity confined to the non-support-bonded polymer fraction which can be extracted from the particles. We must hope, therefore, that the extractable portions are fairly representative of the total silicone phases characterized by the GC tests. With this limitation, GPC can be considered to be a method well suited for defining differences between polymers of similar chemical structure but different history, and it clearly reflects the changes wrought by time and temperature in a chromatographic environment, and also the conditions chosen for polymerization.

The second point to be made concerns the reduction in molecular weight brought about by small amounts of monofunctional monomers, and the branching introduced by trifunctionality, together with its various chromatographic consequences. A demonstration was provided in this study by the IR spectra of low molecular weight fractions of polydimethylsiloxanes which showed significant amounts of trimethylsiloxy groups.

Third, there is the need to avert the formation of cyclic siloxanes, or at least to take the necessary precautions to avoid the loss in critical steps of on-support polymerizations such as the *in situ* synthesis described in this paper. This aspect is, of course, quite different from the requirements of "regular" silicone chemistry.

Finally, an overall comparison of the two methods of on-support polymerization, *in situ vs.* the fluidized bed[1,2], would seem to give preference to the latter in terms of flexibility and support-bonding. The fluidized bed also appears to hold a slight advantage in terms of chromatographic performance. The *in situ* approach, however, is simpler, and definitely one to consider under favorable circumstances.

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