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CROSSLINKED POLYMETHYLPHENYLSILOXANES AS ADSORBENTS FOR GAS CHROMATOGRAPHY

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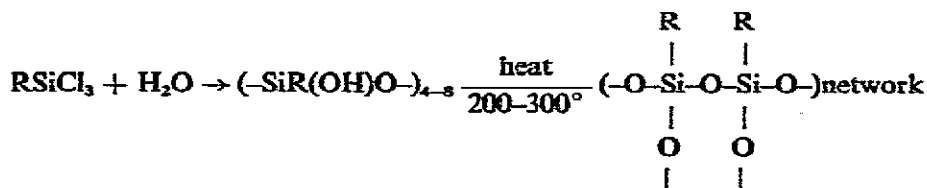
SUMMARY

Crosslinked polymethylphenylsiloxanes that are suitable as adsorbents for gas-solid chromatography have been prepared. These new materials are characterized and evaluated as chromatographic supports. Their chromatographic properties are compared to OV-17, a linear polymethylphenylsiloxane, often used as a liquid phase in gas-liquid chromatography. Scanning electron micrographs show that the materials resemble agglomerates of tiny spheres. The materials have surface areas around 5 m²/g and are thermally stable up to 350°. Small, polar compounds are eluted very early in columns prepared with these adsorbents in a manner similar to macroporous polymers like the Porapaks. Separations of chlorinated benzenes and phenols at temperatures up to 270° are shown.

INTRODUCTION

Linear polysiloxanes, better known as silicones, are among the most popular liquid phases for gas-liquid chromatography (GLC). Attempts to prepare cross-linked polysiloxanes for use in gas-solid chromatography (GSC) have not been as successful. Al-Taiar and co-workers¹ prepared a wide variety of crosslinked polysiloxanes by hydrolyzing organotrichlorosilanes and found that octadecyltrichlorosilane, when hydrolyzed in the presence of small amounts of silicon tetrachloride, gave suitable chromatographic adsorbents. Methyltrichlorosilane and phenyltrichlorosilane and several other silanes did not yield suitable chromatographic adsorbents. Guillot and co-workers² prepared polyphenylsiloxane ladder polymers that were stable to 420° and showed good chromatographic properties. The work of Brown^{3,4} and others⁵ indicates that crosslinked polysiloxanes, known as polysilsesquioxanes, can have a variety of structures depending on reaction conditions. Hydrolysis of trihaloorganosilanes in strong bases or acids is considered to give highly crosslinked networks. It is of interest to note that crosslinked polysiloxanes have surfaces that resemble those of surface-modified silica gels⁶. The former, however, have a considerable amount of surface hydroxyl groups formed during the reaction. In the latter, the surface hydroxyls are utilized to attach organic groups via Si-O or C-O linkages.

Polysilsesquioxanes are basically network polymers commonly prepared as shown by the following equation:



R is usually methyl, phenyl, vinyl, octadecyl or cyanopropyl. The intermediate is usually a low-molecular-weight oil. Hernández⁷ has evaluated methyl and phenyl silsesquioxanes, prepared using the two-step procedure shown, and found that the materials were unsuitable as gas chromatographic adsorbents. These materials, however, showed more promise as adsorbents for normal and reversed-phase liquid chromatography. It should be mentioned that Brown, as mentioned above, has studied the hydrolysis products of organosilanes under many different conditions and does not always postulate random networks for these materials.

In this study, we report the preparation and evaluation of methyl and phenyl silsesquioxanes suitable for GSC. The synthetic procedure resembles the one used by Unger and co-workers^{8,9} to prepare porous silica and involves the hydrolysis of mixtures of methyl- and phenyltrichlorosilane in aqueous ammonium hydroxide.

EXPERIMENTAL

Methyltrichlorosilane (MTCS) and phenyltrichlorosilane (PTCS), purchased from Aldrich (Milwaukee, Wisc., U.S.A.), were used as received. The polymers were prepared by mixing 0.044 mole of MTCS and 0.044 mole of PTCS in a dropping funnel equipped with a PTFE stopcock. The mixture was added dropwise to a well-stirred solution composed of 25 ml of concentrated ammonium hydroxide (58%) (Malinckrodt, St. Louis, Mo., U.S.A.) and 175 ml of distilled water. The reaction is carried out in a well-ventilated hood and controlled by varying the rate of addition of the silanes. A white precipitate is formed as soon as the drop of silanes hits the solution, and a cloud of NH_4Cl forms on the surface of the solution. If the silanes are added too rapidly, the cloud of NH_4Cl rises in a spectacular manner. Upon addition of all of the reactant, the temperature of the solution increases from room temperature to about 55°. The reaction mixture is stirred for 30 min and is filtered, washed with water and then acetone several times, and dried overnight at 120°. The product is then crushed and sieved. The yield is 75% based on $\text{RSiCl}_3 \rightarrow (\text{RSiO}_3)_n$.

Infrared (IR) spectra of the products were obtained using KBr discs. Surface analyses were performed by the Micromeritics Company, Atlanta, Ga., U.S.A. Stainless-steel tubes (1 m \times 1/8 in. I.D.) were used to prepare the columns for GC. A Varian Aerograph A-90-P3 chromatograph equipped with a thermal conductivity detector was used in this study.

RESULTS AND DISCUSSION

A partial characterization of the adsorbents that were prepared was carried out using IR spectroscopy. Fig. 1 shows IR spectra obtained for solids prepared from MTCS, PTCS and from a 50:50 (mole%) mixture of MTCS and PTCS. A careful comparison of these spectra with those reported for linear polysiloxanes OV-17 (50% methyl-50% phenyl) and SE-52 (95% methyl-5% phenyl)¹⁰ reveals that there is very little difference between the solids that were obtained in this work and their linear counterparts. The most important difference is the broad Si-OH band seen in all of our samples. All of the materials presented very strong absorption bands at 1000-1130 cm^{-1} characteristic of the Si-O-Si asymmetric stretching vibration. Silsesquioxanes show a somewhat broader band than linear polysiloxanes in the 1000-1150 cm^{-1} region. The Si-methyl (775 and 1265 cm^{-1}) and the Si-phenyl (690, 732, 1428, 1590 cm^{-1}) absorptions, as well as the broad Si-OH (3100-3600 cm^{-1}) bands, are easily identified from these spectra. The Si-OH absorption bands remained unchanged after heating the KBr discs for several hours at 80°. Although the materials have both polar (Si-OH) and non-polar groups (Si-methyl and Si-phenyl), their most striking property appears to be that of water repellency as is common for the

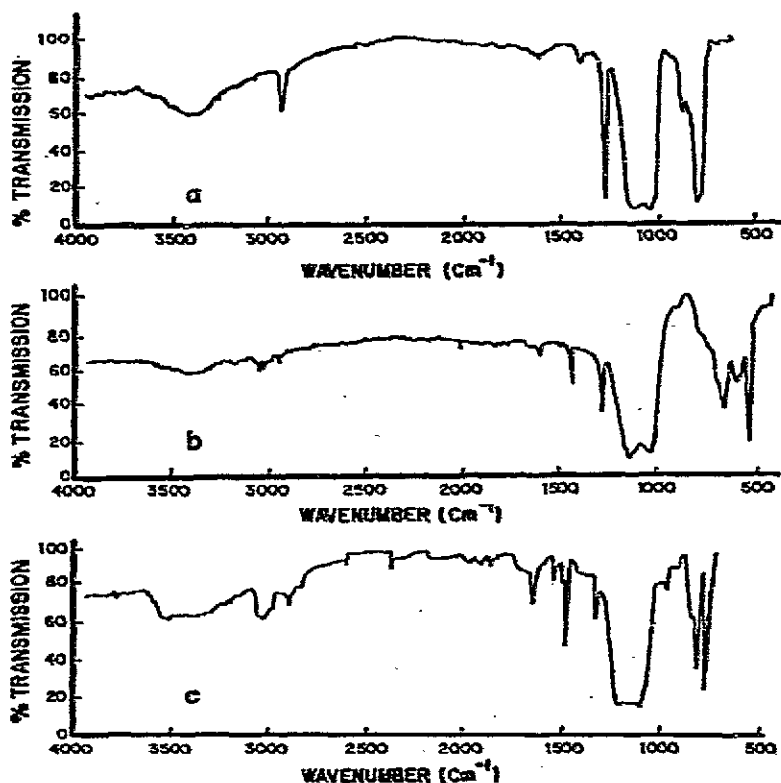


Fig. 1. IR spectra of adsorbents prepared from (a) 100% methyltrichlorosilane, (b) 50:50 (mole %) methyltrichlorosilane and phenyltrichlorosilane and (c) 100% phenyltrichlorosilane.

majority of silicone oils. Although silsesquioxanes having structures known as cubic octamers and dodecamers have been studied by IR, the differences in IR spectra between these compounds and linear and cyclic siloxanes are such that band overlap¹¹ does not allow us to give any structural details of the materials that were obtained.

Fig. 2A and B show scanning electron micrographs that are typical of the materials that were obtained. The irregularly shaped particles are agglomerates of spheres having diameters less than $1\ \mu\text{m}$. These materials have a structure that resembles that of the materials prepared by the *in situ* polymerization of polyols and isocyanates to give polyurethanes^{12,13}. Basically, the materials appear to have interconnecting macropores between bunches of little spheres. In some areas the tiny spheres are very irregular and appear to be of varying sizes.

The properties of four of the adsorbents prepared are listed in Table I. Three of the adsorbents were prepared by dissolving MTCS and PTCS in different amounts of nonane and then hydrolyzing the mixture as described in the experimental section. The packed densities and the surface areas are similar to those of the Chromosorbs A and T produced by Johns-Manville (Denver, Colo., U.S.A.). Kiselev¹⁴ has prepared

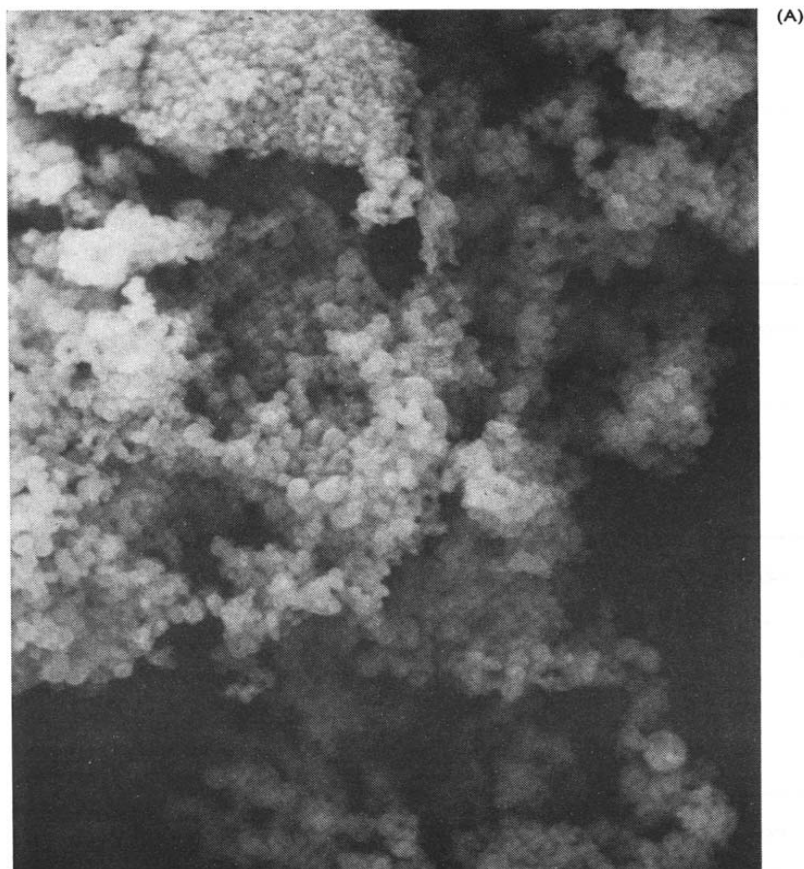


Fig. 2.

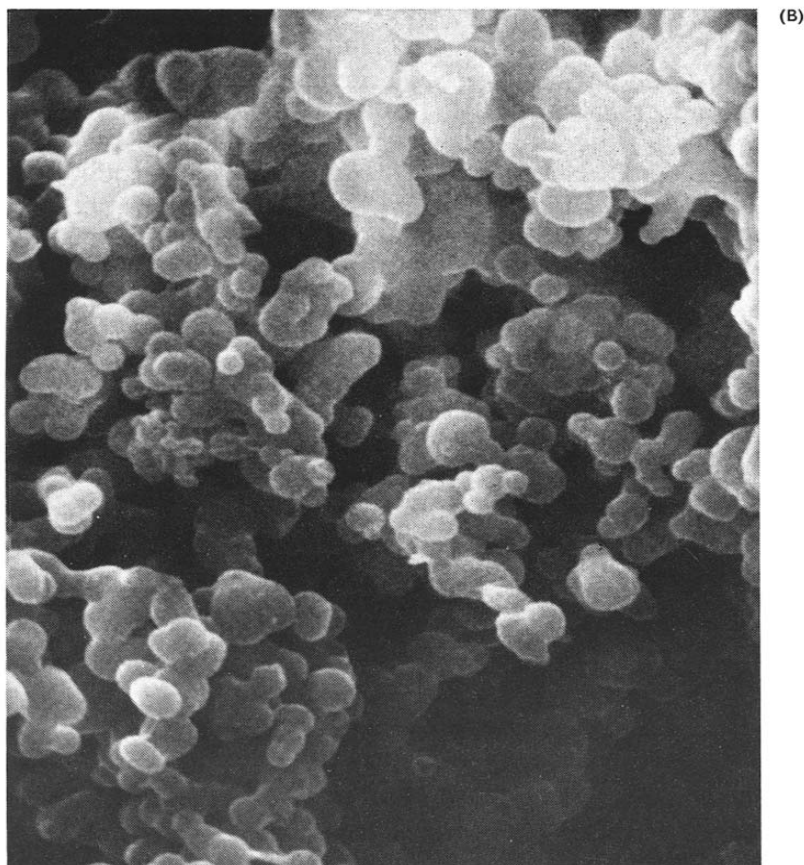


Fig. 2. Scanning electron micrographs of adsorbent 4 at magnifications of (A) $\times 1000$ and (B) $\times 3000$.

silica gels from silicate solutions by precipitation using strong acids. Materials obtained by precipitation from strong acids or bases are generally classified as inhomogeneously porous by Kiselev. He describes his materials as being chalky and containing many, strongly-adsorbing, fine pores which makes the materials unsuitable as GC adsorbents. As will be shown later by the chromatographic data, our materials do not appear to fit this classification.

TABLE I

PROPERTIES OF ADSORBENTS PREPARED FROM EQUIMOLAR AMOUNTS OF MTCS AND PTCS

<i>Adsorbent</i>	<i>MTCS/PTCS (ml)</i>	<i>Nonane (ml)</i>	<i>Packed density (g/ml)</i>	<i>Surface area (m²/g)</i>
1	5/7	0	0.4	5.2
2	5/7	2	0.3	4.1
3	5/7	5	0.2	4.7
4	5/7	10	0.2	6.6

All of the materials have excellent thermal stability up to 350°, after conditioning the materials in packed columns overnight. A column packed with adsorbent 4 was used at temperatures up to 350° without experiencing any changes in baseline. The thermal stability in air of adsorbent 4 is shown in Fig. 3 by the weight loss versus temperature curve. The material lost about four percent of its weight in air at 400°. Differential scanning calorimetry indicated that at 180° there was a small endotherm for this material. All of the materials showed a weight loss at this temperature that amounted to less than one percent.

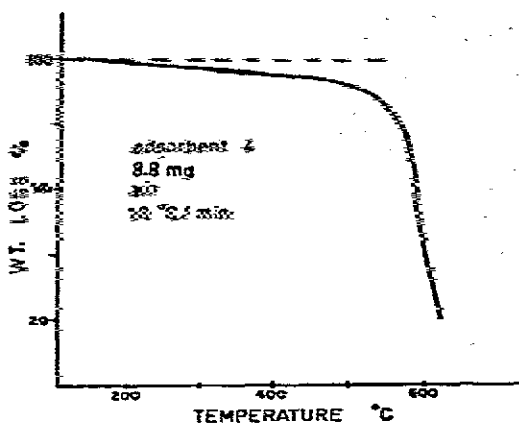


Fig. 3. Weight loss versus temperature curve for adsorbent 4 in air (8.8 mg sample).

The performance of columns prepared from OV-17 and adsorbents 1 and 4 (see Table I) is shown in Figs. 4-6. OV-17 was chosen to compare our materials to a linear polymethylphenylsiloxane that contained equimolar amounts of methyl and phenyl groups. Supelcoport 80-100 mesh (Supelco, Bellefonte, Pa., U.S.A.) coated with 3% of OV-17 was utilized for this purpose. Our materials were sieved to give particles between 120 and 180 μ m. The columns were packed using conventional techniques.

A mixture of water, methanol (1), acetone (2), and *n*-propanol (3) (the numbers in parentheses identify the compounds on the chromatograms) was used to test the polarity of the columns at a temperature of $110 \pm 2^\circ$ and a helium flow-rate of 25 ml/min. OV-17 did not separate this test mixture, while adsorbents 1 and 4 did as is shown in Figs. 5a and 6a, respectively. Adsorbent 1 separates all four components, while adsorbent 4 does not distinguish between water and methanol at this temperature. The same is true for adsorbents 2 and 3 listed in Table I. Both materials, 1 and 4, perform in a manner similar to that of porous polymers such as the Porapaks, which have been used extensively with small polar molecules that tend to tail severely in many chromatographic systems¹⁵. These adsorbents can be considered non-polar although IR spectroscopy indicates that the materials have silanol groups. Under the conditions specified, the column prepared from adsorbent 1 gave a height equivalent to a theoretical plate (HETP) of 14 mm for *n*-propanol, while the column prepared from adsorbent 4 gave a HETP of 7 mm. A porous terpolymer prepared from methylmethacrylate, 2-hydroxyethylmethacrylate and ethylenedimethacrylate

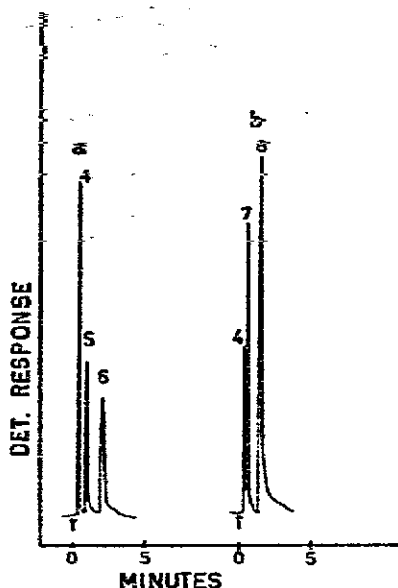


Fig. 4. (a) Chromatogram of chlorobenzene (4), 1,2-dichlorobenzene (5) and 1,2,4-trichlorobenzene (6) on OV-17 at 110°. (b) Chromatogram of chlorobenzene (4), bromobenzene (7) and nitrobenzene (8) on OV-17 at 110°.

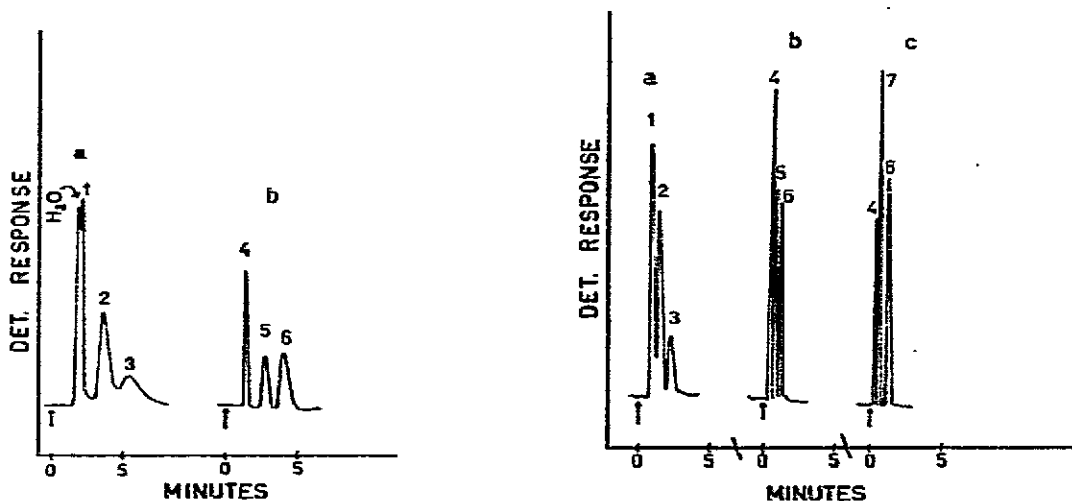


Fig. 5. (a) Chromatogram of water, methanol (1), acetone (2) and *n*-propanol (3) on adsorbent 1 at 110°. (b) Chromatogram of chlorobenzene (4), 1,2-dichlorobenzene (5) and 1,2,4-trichlorobenzene (6) on adsorbent 1 at 235°.

Fig. 6. (a) Chromatogram of methanol (1), acetone (2) and *n*-propanol (3) on adsorbent 4 at 110°. (b) Chromatogram of chlorobenzene (4), 1,2-dichlorobenzene (5) and 1,2,4-trichlorobenzene (6) on adsorbent 4 at 235°. (c) Chromatogram of chlorobenzene (4), bromobenzene (7) and nitrobenzene (8) on adsorbent 4 at 235°.

gave an HETP of 3 mm for *n*-propanol at 175° at a carrier flow of 25 ml/min when used as an adsorbent for GSC¹⁶. Compared to this acrylic terpolymer, the materials reported here perform adequately.

A series of aromatic compounds was also used to evaluate further the nature of these materials. Chlorobenzene (4), 1,2-dichlorobenzene (5), and 1,2,4-trichlorobenzene (6) were first separated on the OV-17 column (Fig. 4a) at 110° using a carrier flow of 25 ml/min. These chlorobenzenes were also separated on adsorbents 1 and 4 at $235 \pm 5^\circ$ using a carrier flow of 20 ml/min, as is shown in Figs. 5b and 6b, respectively. An HETP of 3 mm was obtained for 1,2,4-trichlorobenzene on OV-17, and an HETP value of 5 mm was obtained for both adsorbents 1 and 4 with this same compound. The resolution factors between 1,2-dichlorobenzene and 1,2,4-trichlorobenzene were 3.7, 1.5 and 1.3 for OV-17, for adsorbents 1 and 4, respectively. Both HETP values and resolution factors indicate that the performance of our materials is almost as good as that of a commercial material used in conventional GLC. The polarity of our materials is very close to that of OV-17 when used at temperatures about 100° higher. This fact is also brought out in the separation of chlorobenzene (4), bromobenzene (7), and nitrobenzene (8) as shown for OV-17 in Fig. 4b and in Fig. 6c for adsorbent 4. By proper selection of temperature and flow-rate, it was almost possible to superimpose the chromatograms showing the latter separations.

Slight differences can be seen in the performance of the four adsorbents shown in Table I. By hydrolyzing the mixture of trichlorosilanes in the absence of nonane and in varying amounts of nonane, we felt that the porosity of the material would be changed. However, presently we can not separate the effect of the solvent on the geometric nature of the materials or of the effect on chemical structure.

Adsorbents 5, 6 and 7 were prepared to investigate the effect of varying the concentration of phenyl groups on the selectivity of these materials. Table II shows the conditions utilized to prepare these materials.

TABLE II

ADSORBENTS PREPARED FROM MTCS AND PTCS USING A CONSTANT AMOUNT OF NONANE

Adsorbent	PTCS/MTCS (moles)	PTCS ÷ MTCS (ml)	Norane (ml)
5	2.2/1.0	10	10
6	0.7/1.0	10	10
7	0.3/1.0	10	10

Fig. 7A, B and C compare the chromatographic behaviour of adsorbents 5, 6 and 7, respectively. A test mixture of water, methanol (1), acetone (2), and *n*-propanol (3) was utilized to determine the polarity of these materials at 100° and at a carrier flow of 25 ml/min. The three materials are slightly different, but all behave about the same toward these highly polar compounds. At this temperature, considerable tailing is observed, but at higher temperatures adsorbents 5, 6 and 7 behave like adsorbents 1-4. A mixture of acetone (4), phenol (5), 2-methylphenol (6), 3-bromophenol (7), and 4-methoxyphenol (8) were separated at 270° with adsorbents 5 and 6, and at 245° with adsorbent 7, as shown in Fig. 7D, E and F. Adsorbent 7,

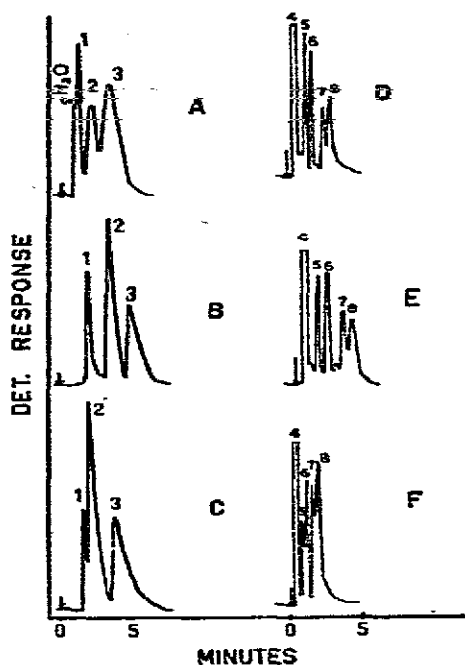


Fig. 7. A, B and C, Chromatograms of water, methanol (1), acetone (2) and *n*-propanol (3) on adsorbents 5, 6 and 7, respectively at 100°. (See Table II for composition of the adsorbents.) D, E and F, Chromatograms of acetone (4), phenol (5), 2-methylphenol (6), 3-bromophenol (7) and 4-methoxyphenol (8) on adsorbents 5, 6 and 7, respectively. Chromatograms D and E were taken at 270° and chromatogram F was taken at 245°.

which contains the least phenyl groups, barely distinguishes the five components (Fig. 7F) at a lower temperature. Adsorbents 5 and 6 separate the phenol mixture very nicely, as shown in Fig. 7D and E, respectively. In the linear polymethylphenylsiloxanes used as liquid phases for GLC an increase in the phenyl content produces a more polar phase. In our materials, the same appears to be true for adsorbents 6 and 7, which have less than 50 mole percent of phenyl groups. At the highest mole ratio of phenyl to methyl groups, the trend seems to reverse somewhat and thus material 5 does not appear as polar as 6. Hernandez⁷ has observed that the smaller methyl groups produce tighter networks. It is possible that a greater amount of the bulkier phenyl group gives a network with slightly different properties.

All of the adsorbents were also evaluated with hydrocarbon mixtures. These materials did not separate well the linear alkanes and performed adequately with benzene, toluene, and xylene. Adsorbent 4, for example, gave an HETP of 7 mm with benzene at a column temperature of 120° using a carrier flow of 25 ml/min. This HETP value compares favorably with those obtained by Di Corcia *et al.*¹⁷ who obtained a value of 5 mm for benzene using graphitized carbon black modified with 2,4,5,7-tetranitrofluorenone at 187° using a carrier flow of 11.7 ml/min and Onuska *et al.*¹⁸ who obtained using Chromosorb P coated with caesium chloride a value of 10 mm for benzene at 230° with a carrier flow of 49 ml/min. In general, the materials that we prepared seem to separate polar or moderately polar compounds better than non-polar compounds.

CONCLUSIONS

In summary, we have prepared crosslinked polymethylphenylsiloxanes that are useful as adsorbents for GSC. These materials behave almost like their linear counterpart does in GLC. The reaction that we used to produce these materials is both straightforward and reproducible. Kiselev and Yashin¹⁹ suggest that solid chromatographic supports need to satisfy the following six requirements: (1) the materials must be free from micropores and their macropores need to communicate via large holes, (2) the specific surface area should be in the range of 1 to 10 m²/g, (3) the materials must be chemically inert, (4) they must absorb weakly and unspecifically, (5) they should be thermally stable up to 350°, and (6) the particles should be smooth, of small size and of good mechanical strength. There is no doubt that these requirements are difficult to meet and presently there is no ideal adsorbents for GSC. Our materials seem to satisfy nearly all of the requirements mentioned. We are currently in the process of determining the pore structure and evaluating the materials with different families of compounds. Finally, we feel that the materials reported here have a good potential as supports for GSC. Some questions relating to the chemical structure of these materials as well as others require further study.

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