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Surface Characterization of Methylsilsesquioxane–Phenylsilsesquioxane Copolymers

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ABSTRACT: Mixtures of methyl- and phenyltrichlorosilanes have been hydrolyzed to obtain cross-linked polysiloxanes, often referred to as polysilsesquioxanes. Glassy or amorphous materials are obtained, depending on the reaction conditions used. Infrared spectroscopy, scanning electron microscopy, and gas chromatography have been employed to study the surface characteristics of these materials. The infusible solids that are obtained are thermally stable up to 400 °C. Surface areas for the materials range from 0.02 to 5 m^2/g, depending on the reaction conditions. Swelling experiments show that the materials are very tightly cross-linked networks. The soft materials having surface areas around 5–10 m^2/g are suitable as adsorbents for gas–solid chromatography.

Introduction

The chemistry of linear poly(dimethylsiloxanes) and poly(methylphenylsiloxanes) has been studied extensively. Highly cross-linked poly(methylphenylsiloxanes), often referred to as poly(methylphenylsilsesquioxanes), are less widely known. Polysilsesquioxanes are generally prepared by hydrolysis of organotrichlorosilanes. Gilliam and coworkers[1] described the resinous products obtained by the cohydrolysis of dimethylchlorosilane and methyltrichlorosilane in the early 1940s. Cross-linked poly(alkylsiloxanes) were first made by Ladenberg in 1872; however, Kipping[3] is credited with proposing the siloxane bond and the formation of linear and cross-linked polymers in 1914. Patnode and Wilcock[4] recognized that linear, soluble compounds are formed during the hydrolysis of methyltrichlorosilanes in certain solvents. Brown and co-workers,[5–7] after extensive studies, reported that hydrolysis of organotrichlorosilanes gave very complex structures. Slinyakova and Niemark[8] reported that few investigations dealing with methods of obtaining gels from organosilicon compounds appear in the Russian literature prior to 1962. Many of the studies dealing with silsesquioxanes up to about 1970 involved the synthesis and characterization of low and high molecular weight polymers.[9–11] Andrianov and his group, however, have investigated extensively many aspects of different silsesquioxanes, including their morphology,[12] conformations,[13] thermal decomposition,[14] hydrodynamic and optical properties,[15] and synthesis.[16]

After the introduction of surface-modified silica gels in the field of chromatography, research groups evaluated polysilsesquioxanes as adsorbents for gas–solid and liquid–solid chromatography. Although poly(phenylsilsesquioxane)[17] and poly(octylsilsesquioxane)[18] have been reported to be useful as adsorbents, poly(methyl-, -phenyl-, and -methylphenylsilsesquioxane) copolymers have been

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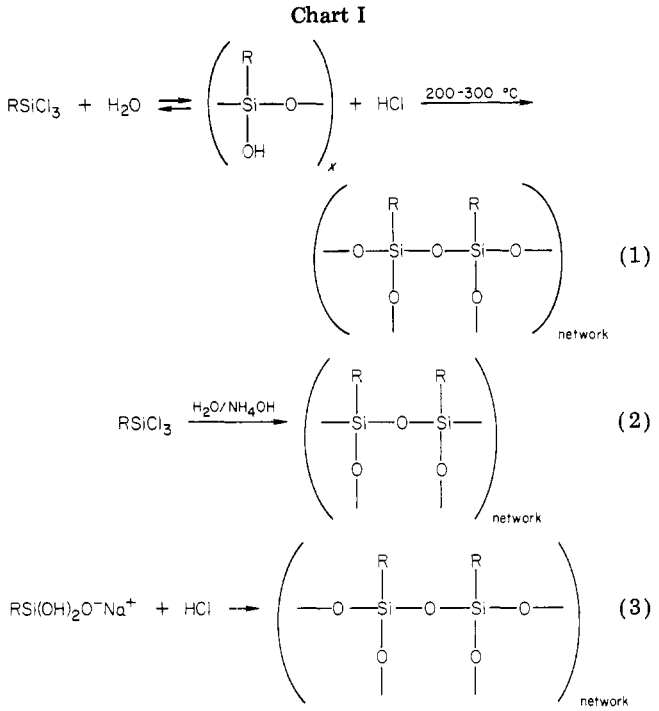
Chart I



shown by other workers[17,19] to have very poor chromatographic properties. More recently, it has been shown that cohydrolysis of methyl- and phenyltrichlorosilanes under some reaction conditions yields solids with good chromatographic properties.[20] Ivanova[21] has also suggested the use of polysilsesquioxanes as sorbents for liquid chromatography.

Silsesquioxanes can be prepared by the synthetic routes shown in Chart I. Hydrolysis of mixtures of methyl- and phenyltrichlorosilanes in water yields low molecular weight materials that are soluble in acetone. Presumably, the acid produced in reaction 1 can hydrolyze the product formed so that x = 4–8, depending on the R group, pH, solvent, and temperature.[6] If the intermediate siloxane is separated from the water, purified, and then heated for several hours in air or nitrogen, a hard, glassy solid is produced. Reaction 2, on the other hand, yields amorphous materials directly. Reaction 3 was first reported by Slinyakova,[8,22] who has produced xerogels having surface areas between 200 and 500 m^2/g.

In this report, the synthesis and surface characterization of materials produced by using the synthetic procedures 1 and 2 described in Chart I are presented in an effort to shed some light as to why adsorbents from polysilsesquioxanes often behave so differently. Polysilsesquioxanes prepared primarily from equimolar amounts of methyltrichlorosilane and phenyltrichlorosilane were used in this study.

Experimental Section

Methyltrichlorosilane (MTCS) and phenyltrichlorosilane (PTCS) purchased from Aldrich were used as received. In a typical reaction equimolar amounts (usually 0.044 mol) of MTCS and PTCS were mixed in a dropping funnel equipped with a Teflon stopcock. The mixture was added dropwise to a large volume (400 mL) of deionized water. The reaction is carried out in a well-ventilated hood and controlled by varying the rate of addition of the silanes. After the addition of the silanes is complete, the solution is stirred for 1 h and the water is decanted from the waxy material produced. The waxy product is washed repeatedly with water and allowed to dry in air. A yield of 80% is obtained, based on the assumption that $RSiCl_3 \rightarrow (RSiO_{3/2})_n$. The materials obtained were then dried at 150 °C in air for 24 h and at 300 °C for another 24 h. All the products obtained by procedure 1 were hard, glassy materials.

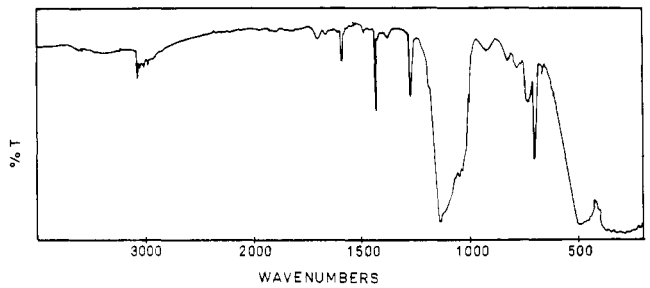


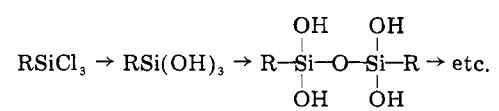
Figure 1. Infrared spectrum of acetone-soluble poly(methylphenylsilsesquioxane).

The polymers obtained by procedure 2 were also prepared by the cohydrolysis of MTCS and PTCS in a solution composed of 25 mL of ammonium hydroxide (Mallinckrodt, 58%) and 175 mL of deionized water. The silane mixture was added dropwise to a well-stirred solution and the reaction was controlled by the rate of addition of the silanes. A white precipitate is formed as soon as a drop of silane hits the basic solution and a cloud of NH_4Cl forms on the surface of the solution. The cloud of ammonium chloride rises in a spectacular manner if the silanes are added too rapidly. During the addition of all the reactants, the temperature of the solution increases from room temperature to about 55 °C. The reaction mixture is stirred for 30 min and filtered. The solid material is washed well with water and acetone and dried overnight at 120 °C. All of the materials obtained by this procedure were amorphous. The yield of materials is slightly less than that obtained in procedure 1. Apparently, acetone dissolves some of the material that precipitates in the reaction.

The products that were obtained were characterized by infrared spectroscopy. Transmission spectra of films cast from acetone and of insoluble solids as KBr disks were obtained with a Perkin-Elmer 283B spectrometer. A Perkin-Elmer multiple internal reflection accessory was also used to study these materials. Scanning electron micrographs were obtained, after gold-shadowing the specimens, with a Philips SEM 501b instrument. Nitrogen adsorption isotherms for the hard, glassy materials were performed by Quantachrome Corp. and for the amorphous materials by Micromeritics Co. The evaluation of the materials by gas chromatography was carried out by packing 70–80 mesh particles in a $^1/_8$-in. o.d. stainless steel column 1 m long. A Varian Aerograph A-90-P3 chromatograph equipped with a thermal conductivity detector was used in this study. Swelling experiments were carried out by packing 4 mm × 250 mm stainless steel columns and measuring the pressure required to obtain a flow of 1 mL/min with different solvents. A Waters ALC 200 liquid chromatograph was used for this part of the study.

Results and Discussion

Hydrolysis of organohalosilanes is known to proceed through a series of steps. The reaction sequence can be shown as follows:



Depending on reaction conditions as well as on the R group present, a variety of products can form once the silanols start condensing. Hydrolysis of mixtures of MTCS and PTCS in water gives an oily product that, upon standing, gives a brittle, infusible material. Figure 1 shows an IR spectrum of a low molecular weight, acetone-soluble poly(methylphenylsiloxane). The IR spectrum was obtained by casting a thin film on a NaCl plate from acetone. This spectrum is almost identical with that of a linear poly(methylphenylsiloxane).[20] The infrared spectrum of thicker films of this acetone-soluble material clearly shows the free-hydroxyl (Si–OH) band at 3640 cm^{-1} and a broad band at 3200–3500 cm^{-1} due to hydrogen bonding of the silanol groups. The shape of the asymmetric Si–O–Si band

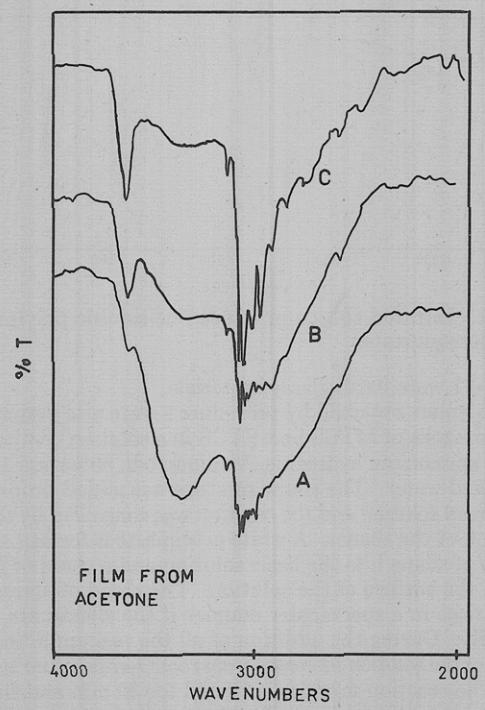


Figure 2. Infrared spectra of thermally treated acetone-soluble poly(methylphenylsilsesquioxane): trace A, original spectrum; trace B, spectrum obtained after heating sample shown in A for 3 min at 130 °C; trace C, spectrum obtained after heating sample shown in B for 20 min at 130 °C.

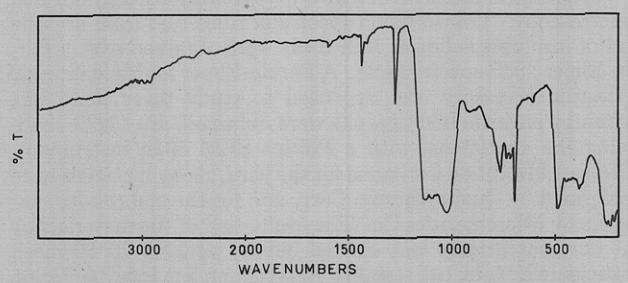


Figure 3. Multiple internal reflectance IR spectrum of infusible and insoluble poly(methylphenylsilsesquioxanes).

at 1030–1160 cm^{-1} is identical with that published by Anderson[23] for a $CH_3SiO_{3/2}$ hydrolysate. Figure 2 shows the changes produced in the 2000–4000-cm^{-1} region of the spectrum of the acetone-soluble material as it is heated. The traces shown in Figure 2 were obtained by casting a thick film of the acetone-soluble poly(methylphenylsiloxane) on a NaCl plate and heating the plate for 3 min at 130 °C (trace B) and then for 20 min at 130 °C (trace C). Trace A was obtained at room temperature after evaporating the solvent. After the heat treatment the material was not soluble in acetone. Presumably, cross-linking of some of the silanol groups occurs upon heating. This is shown by the disappearance of the broad SiOH band due to hydrogen bonding. The absorption band due to the free silanol groups apparently increases as the broad band due to hydrogen bonding disappears.

Figure 3 shows a typical multiple internal reflectance IR spectrum of the solid, infusible materials obtained by either procedure 1 or 2. Generally, it was found that the spectra of the infusible solids differed from that of the acetone-soluble product in the 3200–3500-cm^{-1} region and in the shape of the asymmetric Si–O–Si bands at 1030–1160 cm^{-1}.

The thermal stability of the infusible solids obtained by either procedure was also nearly the same. Differential scanning calorimetry showed that a small endotherm occurred at 180 °C when these materials were heated. The endotherm was slightly larger for the amorphous materials, although thermal gravimetric analyses showed that the weight loss that occurred at 180 °C was less than 1% for the materials. At 400 °C the materials lose about 3% of their weight and at 515 °C, they lose 10% of their weight in air.

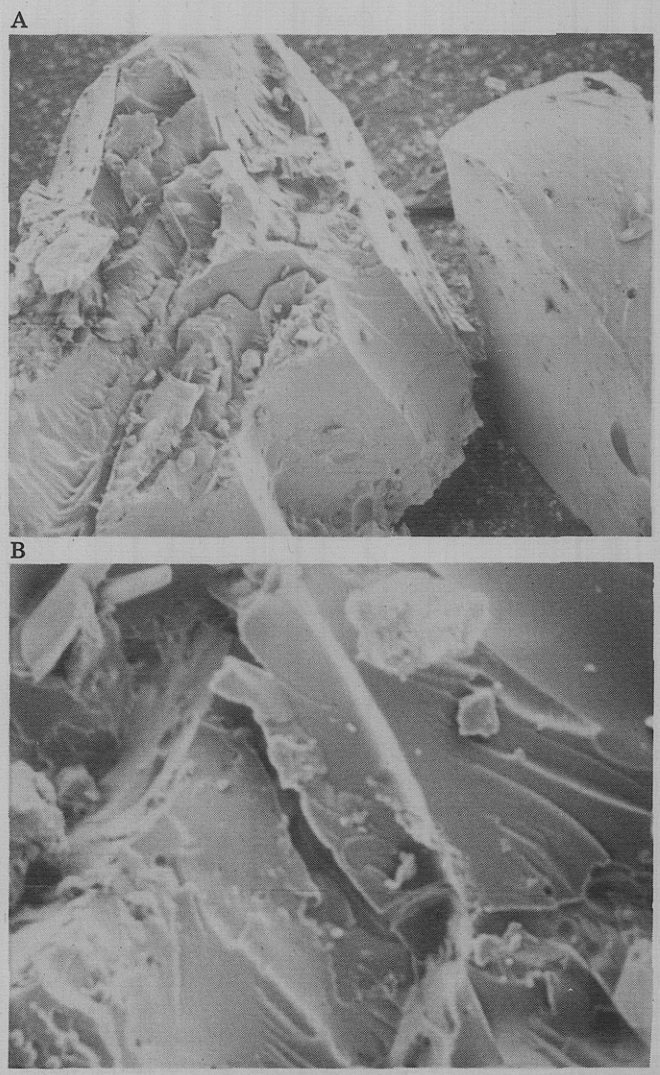


Figure 4. Scanning electron micrographs of hard, glassy solids at magnifications of 320× (A) and 2500× (B).

Although infrared spectroscopy and thermal analysis show that the chemical composition and the thermal properties of these materials are not influenced by the synthetic method used, scanning electron microscopy shows that the morphology of the materials is affected tremendously. Figure 4 shows electron micrographs of the hard, glassy materials (obtained by procedure 1) at magnifications of 320× and 2500×. Figure 5 shows electron micrographs of the amorphous materials (obtained by procedure 2) at magnifications of 320× and 2500×. The surface area for the material shown in Figure 4A,B was 0.02 m^2/g. The material shown in Figure 5A,B had a surface area of 4 m^2/g. As can be suspected, the material with the lower surface area displayed very poor chromatographic properties, while the material with the larger surface area is useful as an adsorbent for gas–solid chromatography. As can be seen from Figure 6, the glassy materials gave very broad peaks for most compounds except water, while the soft materials gave better resolution for a wide variety of compounds.[20] In general, the materials retain nonpolar materials longer than polar compounds.

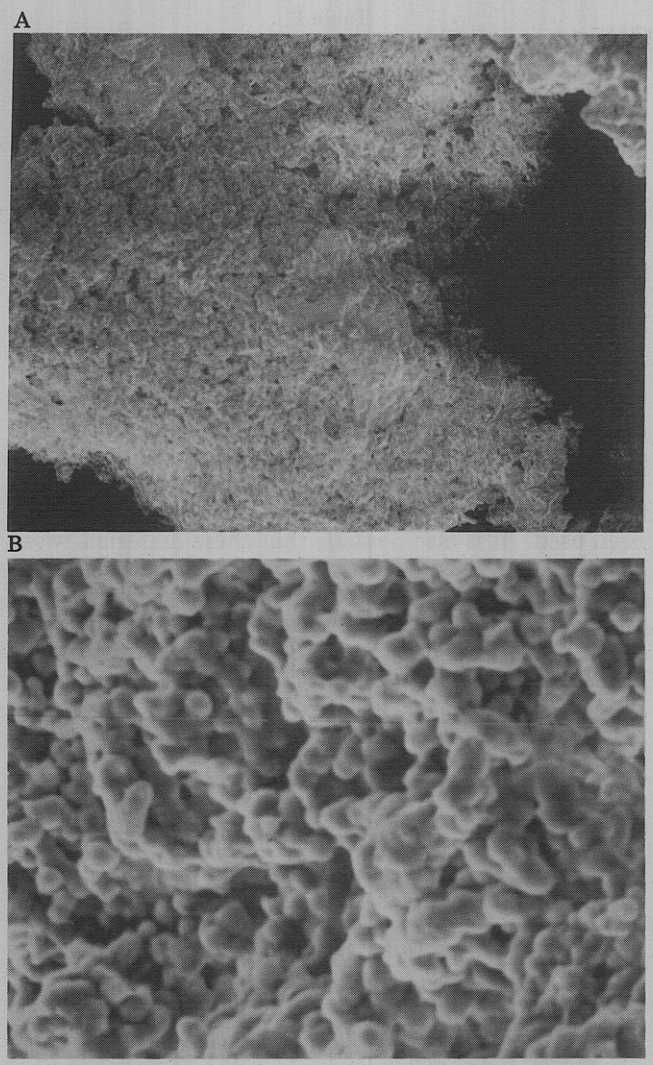


Figure 5. Scanning electron micrographs of amorphous materials at magnifications of 320× (A) and 2500× (B).

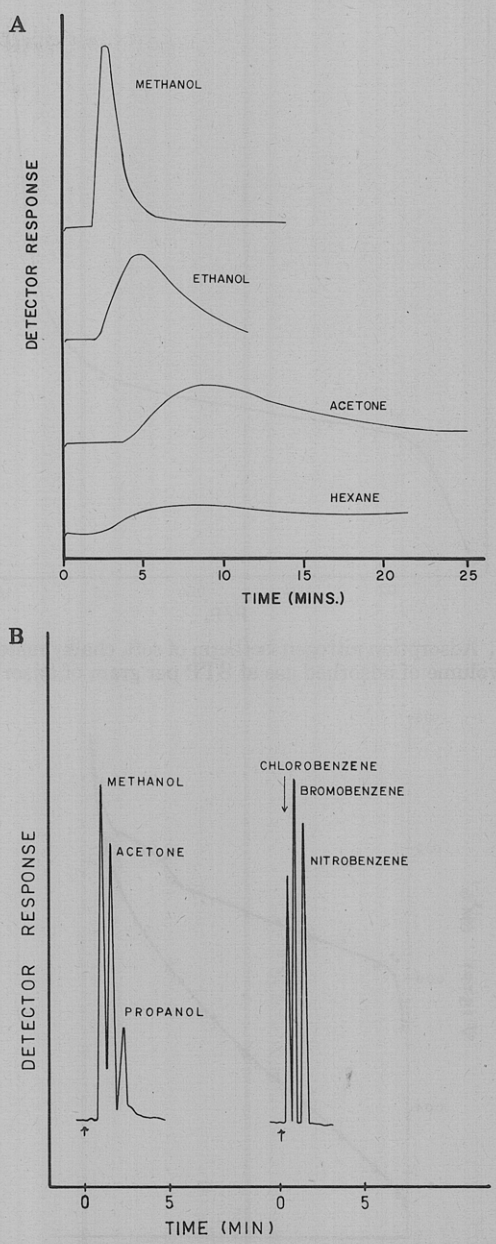


Figure 6. (A) Traces showing typical gas chromatographic behavior of the hard, glassy solids at 110 °C. Conditions: $^1/_8$-in. o.d. × 1-m stainless steel columns, flow 20 mL/min. (B) Traces showing gas chromatographic behavior of the amorphous materials at 110 °C for polar organics and at 235 °C for aromatics. Conditions: $^1/_8$-in. o.d. × 1-m stainless steel columns, flow 20 mL/min.

Nitrogen adsorption isotherms are shown in Figures 7 and 8 for the soft, amorphous material and the glassy material, respectively. The soft material has an adsorption isotherm that resembles that of aerogels[24] and that falls into the Brunauer type II classification.[25] The plateau region of the isotherm is somewhat flatter than in aerogels, probably indicating that after the monolayer coverage is reached only macropores are being filled. The hard and glassy materials, however, have a peculiar adsorption isotherm in that surface coverage is reached at a very low value of relative pressure, but the material continues to strongly adsorb nitrogen. As the desorption isotherm shows, these glassy materials trap the adsorbate very tightly. Although we do not know why the materials desorb in this way, this unusual behavior can account for the poor chromatographic behavior of the materials. If molecules can be trapped by the highly cross-linked gel matrix, this could account for the broad peaks shown in Figure 6A.

Slinyakova[8,22] has obtained adsorption isotherms of hexane, benzene, and methanol vapors on his xerogels and has reported that the materials have a heterogeneous, coarsely porous structure with surface areas ranging from 140 to 270 m^2/g. The adsorption isotherms reported by these Russian workers are often very similiar to those shown in Figure 7. Although adsorption and desorption isotherms often showed a noticeable hysteresis loop, none of the xerogels display a behavior like that shown in Figure 8. These workers report true densities ranging from 1.3 to 1.6 g/cm^3 and apparent densities ranging from 0.4 to 0.8 g/cm^3. We have found that our amorphous materials have true densities of 1.3–1.5 g/cm^3 and apparent densities of 0.4–0.6 g/cm^3. To our knowledge, Slinyakova has not reported on the chromatographic behavior of his gels.

Stainless steel tubes (4 mm × 250 mm) were packed with 80–100-μm particles of the hard, glassy materials in order to study the notion that the materials might behave like gels. Different solvents were pumped through the columns at a flow rate of 1 mL/min. The pressure required to maintain this flow was measured with a Waters ALC 200 pump. Three materials with different compositions are shown in Table I along with the pressures required to achieve a flow of 1 mL/min.

The material prepared with 90% phenyltrichlorosilane and 10% methyltrichlorosilane gave a product that was swollen considerably by chloroform and acetone, which are good solvents for linear, low molecular weight poly(me-

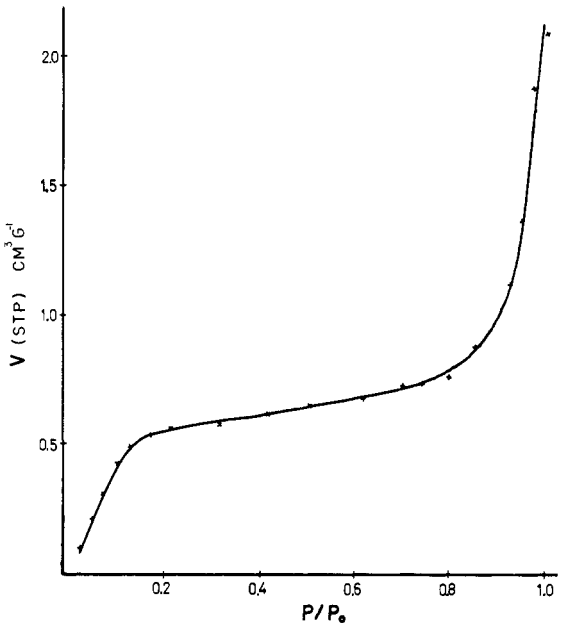


Figure 7. Adsorption nitrogen isotherm of soft, chalky materials. V is the volume of adsorbed gas at STP per gram of adsorbent.

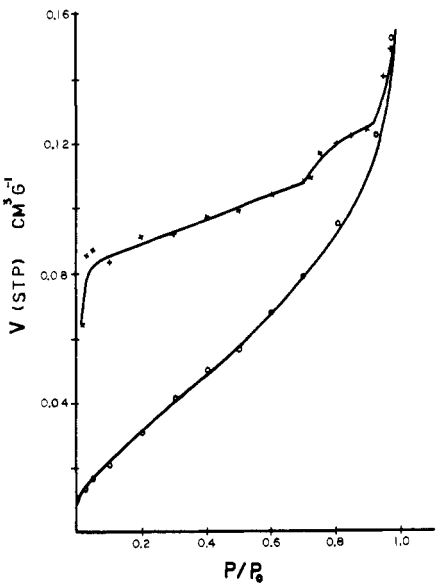


Figure 8. Adsorption nitrogen (O) and desorption (×) isotherms of hard, glassy materials. V is the volume of adsorbed or desorbed gas at STP per gram of adsorbent.

thylphenyl)siloxanes. The larger phenyl group apparently is responsible for a network that is more loosely cross-linked. A similar observation was made by Slinyakova.[22] Apparently, the other two materials do not show any swelling or penetration by solvents. These swelling experiments showed that the poly(methylphenylsilsesquioxanes) prepared from 50% MTCS and 50% PTCS are highly cross-linked, nonswellable networks. Thus, the peculiar behavior of these polysilsesquioxanes may be due to other factors which are presently not known to us. Hernandez[19] has shown that all three materials can be used in reverse-phase and normal-phase chromatography. He showed that the elution pattern for acetone–benzene mixtures could be reversed by going from relatively nonpolar solvents to highly polar solvents.

Table I
Pressures (psi) Required To Maintain a Flow of 1.0 mL/min for Various Poly(methylphenylsilsesquioxanes)

	adsorbents		
solvents	90 PTCS/ 10 MTCS	50 PTCS/ 50 MTCS	20 PTCS/ 80 MTCS
heptane	60	10	10
chloroform	1000	50	50
acetone	290	10	10
acetonitrile–water (1:1)	100	80	80

From this study, it can be concluded that poly(methylphenylsilsesquioxane) copolymers with different chromatographic properties can be prepared, depending on the synthetic procedure that is employed. The differences reported in the literature may arise from the fact that materials with abnormally low surface areas may have been used. It is also possible that these materials when heated under some conditions may yield materials with peculiar adsorption properties. Useful adsorbents, however, can be prepared and further work on these and other silsesquioxanes needs to be performed to fully evaluate the potential of these materials.

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