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1,5-BIS-(*m*-PHENOXYPHENYL)-1,1,3,3,5,5-HEXAPHENYLTRISILOXANE AS A STATIONARY PHASE IN HIGH-TEMPERATURE GAS CHROMATOGRAPHY*

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SUMMARY

The use of 1,5-bis-(*m*-phenoxyphenyl)-1,1,3,3,5,5-hexaphenyltrisiloxane as a stationary phase in high-temperature gas chromatography in the range 40–360°C is reported. Its practical utilization is demonstrated with the separation of mixtures of high-boiling silanes, polynuclear aromatic hydrocarbons, barbiturates and poly(*m*-phenyl ethers).

INTRODUCTION

Siloxane materials are the most widely used liquid stationary phases in gas chromatography today. Their high thermal and chemical stability coupled with low bleed characteristics and the possibility of introducing suitable functional groups to adjust the retention properties have resulted in a considerable number of commercially available products that cover a wide range of applications. This topic has been discussed in several papers[1–4].

Siloxane polymers are usually produced by polymerizing a cyclosiloxane at moderate temperature in the presence of catalysts that must subsequently be removed to prevent depolymerization under gas chromatographic column conditions. Another operation that must be conducted prior to gas chromatography is the removal of relatively volatile low-molecular-weight fractions of the polymer. Both operations, if performed incompletely, cause excessive bleeding of the column and deterioration of its performance.

The introduction of phenyl groups into polysiloxanes that contain only methyl functional groups improves the thermal stability and reduces the volatility of the resulting material. Unfortunately, phenyl groups increase the melting point and adversely affect the separation properties of the stationary phase.

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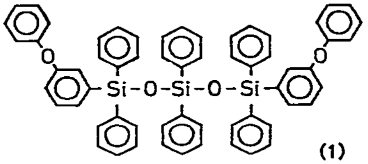
The main objective of this work was to evaluate a new siloxane stationary phase for gas chromatographic purposes. A stationary phase should possess a relatively low temperature of softening, low volatility at relatively high temperatures and high thermal stability, enabling it to be used in the temperature range from ambient to several hundred degrees Celcius without sacrificing its good separation properties. Currently commercially available polysiloxanes consist of molecules with various numbers of the siloxane groups; a preferred stationary phase should be a well defined compound with a precise boiling point, appropriate for the separation of many classes of compounds. Further, with a defined chemical structure and its capabilities for participation in π-type charge-transfer interactions it should be useful for the evaluation for such interactions in solutions.

The dependence of volatility and melting point on the structure of compounds containing silicon was considered in previous papers[5–7]. The methyl and ethyl derivatives of *m*-phenoxyphenyldiphenylsilane are mostly liquids or low-boiling compounds, unlike the corresponding derivatives of the *o*- and *p*-isomers. However, the reverse applies to the pentaphenylphenoxyphenyldisiloxane isomers: the melting point of the *m*-phenoxy isomer is 157–158°C, of the *p*-isomer 95–96°C and of the *o*-isomer 143–144°C. The desirable properties appeared only with trisiloxanes; 1,5-bis-(*m*-phenoxyphenyl)-1,1,3,3,5,5-hexaphenyltrisiloxane (MPHT) (1) was an oily product, in contrast to the corresponding *o*-isomer with a melting point of 114–115°C. Because of its minimal thermal degradation, determined by the thermogravimetric method, this trisiloxane proved to be a convenient stationary phase for gas chromatography.



(1)

In this work we investigated the separating capability of MPHT for various classes of high-boiling compounds. To compare its selectivity with that of other products used for this purpose, the McReynolds constants were calculated.

EXPERIMENTAL

Apparatus

The gas chromatographic measurements were carried out with a Pye Model 64 temperature-programmed chromatograph with dual flame-ionization detectors (Series 104, Pye Unicam, Cambridge, Great Britain). It was equipped with a 0–1 mV recorder (Honeywell Electronik 194). The columns employed were 170 × 0.4 cm I.D. glass tubes and nitrogen was used as the carrier gas at a flow-rate of approximately 30 ml/min. The samples were introduced with a 10-μl Hamilton microsyringe. The injection port and detector were maintained at 370 and 350°C, respectively. The column temperature, either isothermal or programmed, was chosen with respect to the boiling point of the compounds being analysed.

Column packing

MPHT is a transparent, colourless gel soluble in diethyl ether, dichloromethane, chloroform and aromatic hydrocarbons. Some physical constants are given in Table I. It was resistant to most chemicals except strong bases and acids. Its thermal stability has been reported elsewhere[7].

TABLE I

PHYSICAL CONSTANTS OF 1,5-BIS-(*m*-PHENOXYPHENYL)-1,1,3,3,5,5-HEXAPHENYLTRISILOXANE

Empirical formula	$C_{60}H_{48}O_4Si_3$
Molecular weight	917.3
Volatile fractions[7]	0% (340°C), 1% (360°C), 2% (380°C)
Melting point	34–37°C
Boiling point	360–370°C/0.05 Torr
Density	1.084 g/cm^3
Recommended temperature	40–360°C

The packing was prepared in the usual manner by dissolving the stationary phase in chloroform and slurrying it with Chromosorb W AW (45–60 mesh) (Johns-Manville, Denver, CO, U.S.A.); the slurry contained 2% or 20% of the liquid phase. Columns packed with 0.16 or 2.05 g of the stationary phase were pre-conditioned for 8 h at approximately 300°C with the carrier gas flowing and were used both for determining the retention volumes and for calculating the McReynolds constants[8].

Chemicals

The chemicals used were mainly commercial materials of high purity. 2-Phenoxyphenyldiphenylsilane, 3-phenoxyphenyldiphenylsilane, 4-phenoxyphenyldiphenylsilane, 2-phenoxyphenyldiphenylmethylsilane, 3-phenoxyphenyldiphenylmethylsilane, 4-phenoxyphenyldiphenylmethylsilane, 2-phenoxyphenyldiphenylethylsilane, 3-phenoxyphenyldiphenylethylsilane and 4-phenoxyphenyldiphenylethylsilane were synthesized as described previously[5].

RESULTS AND DISCUSSION

The thermal stability of MPHT had been measured thermogravimetrically[7] and the results showed an upper temperature limit of about 360°C. Higher temperatures can be tolerated during a temperature-programmed run. Above this temperature, the stationary phase began to volatilize and/or to undergo thermal decomposition. Unfortunately, thermogravimetric analysis yields indirect data only, which are not suitable for gas chromatographic purposes. As there is no universally accepted method of determining the maximal temperature limit for liquid stationary phases, we chose the procedure described by Novotný and Zlatkis[9]. Comparing the thermal stability of MPHT with that of SE-30, which is considered to be the most stable silicone phase, we found a slightly higher relative bleeding rate with MPHT. Nevertheless, with proper conditioning and on a carefully prepared support it can be used up to 360°C.

The chemical stability of MPHT is limited by the nature of the Si–O–Si bond. It decomposes at higher temperatures in the presence of basic or acidic catalysts, but this limitation applies to all siloxanes. Therefore, base-washed supports should not be used. For high-temperature operation silanized supports should be avoided for reasons that are generally known.

Because the McReynolds constants (ΔI) provide the best information about the selectivity of stationary phases, we made use of this classification. As has been reported[10], an advantage of these constants is their clear physical meaning as the relative sorption equilibrium constants of a solute on a stationary liquid with respect to a standard squalane stationary liquid. Table II gives both the ΔI values obtained on MPHT and those on the silicones OV-11, OV-17 and DC-710. It is evident that MPHT possesses a selectivity similar to those of OV-17 and DC-710 and differs slightly from OV-11. However, the maximal usable temperature of DC-710 is 250°C[11] and OV-17 showed greater bleeding at temperatures above 300°C in our test[7]. We are aware of the temperature difference between the measurements of the ΔI values on MPHT and those on OV-11, OV-17 and DC-710 (120°C). As this work follows a previous contribution[10] on a similar topic, the same conditions were used in the present study.

TABLE II

SELECTED McREYNOLDS CONSTANTS (ΔI)

Solute	ΔI				
	Squalane (142°C)	*MPHT (142°C)*	*OV-11*[8] *(120°C)*	*OV-17*[8] *(120°C)*	*DC-710*[8] *(120°C)*
Benzene	692	135	102	119	107
1-Butanol	638	145	142	158	149
2-Pentanone	671	142	145	162	153
1-Nitropropane	664	324	219	243	228
Pyridine	756	227	178	202	190
2-Methyl-2-pentanol	746	67	100	112	107
1-Iodobutane	855	122	103	119	108
1,4-Dioxane	705	204	164	184	174
cis-Hydrindane	1032	60	59	69	60

MPTH provided efficient separations in various high-temperature applications. Preliminary tests indicated that for such work, a 2% coating provided good stability and separating power. This was demonstrated with the analysis of several different mixtures.

Fig. 1 shows the separation of structurally similar silanes and specific retention volumes are given in Table III. The retention order within the individual triplets corresponds to the boiling points, which is consistent with the general notion of the steric arrangement of silane molecules. Their V_g values (see Table III) seem to be high, but with regard to the low content of the stationary phase in the column the retention times do not exceed the desirable limit. Moreover, by varying the experimental conditions the retentions could be lowered.

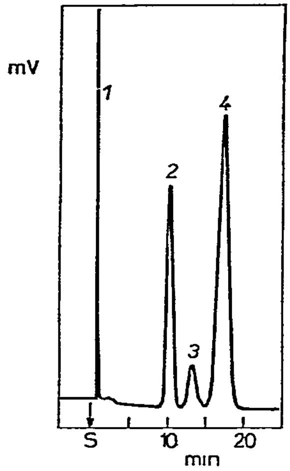


Fig. 1. Separation of high-boiling arylsilanes. Column, 170 × 0.4 cm I.D.; stationary phase, MPHT (2%) on Chromosorb W AW (45–60 mesh); column temperature, 280°C; carrier gas, nitrogen at a flow-rate of 30 ml/min. Peaks: 1 = solvent; 2 = 2-phenoxyphenyldiphenylsilane; 3 = 3-phenoxyphenyldiphenylsilane; 4 = 4-phenoxyphenyldiphenylsilane.

TABLE III

SPECIFIC RETENTION VOLUMES OF SOME STRUCTURALLY SIMILAR HIGH-BOILING SILANES

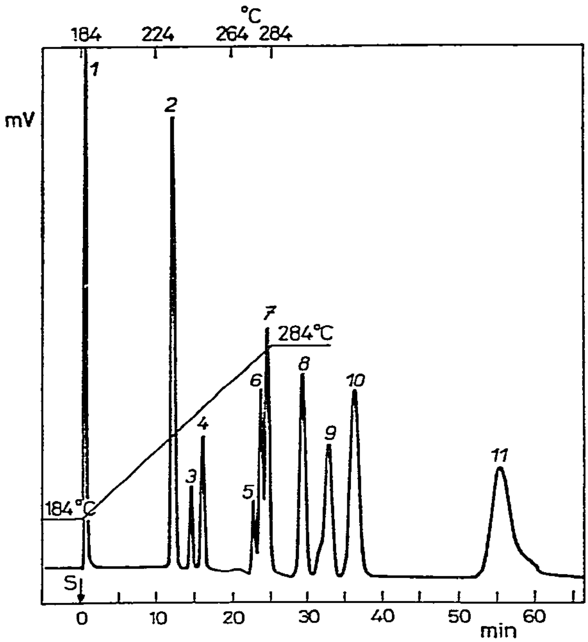
Temperature 280°C; carrier gas, nitrogen.

Compound	*B.p.*[5] *(°C/Torr)*	$r_{1,2}$
2-Phenoxyphenyldiphenylmethylsilane	170–171/0.4	0.75
3-Phenoxyphenyldiphenylmethylsilane	180–182/0.3	1.00
4-Phenoxyphenyldiphenylmethylsilane	195–197/0.5	1.40
V_g (3-phenoxyphenyldiphenylmethylsilane) (ml/g)	—	1070
2-Phenoxyphenyldiphenylethylsilane	173–174/0.4	0.70
3-Phenoxyphenyldiphenylethylsilane	184–186/0.4	1.00
4-Phenoxyphenyldiphenylethylsilane	198–201/0.5	1.30
V_g (3-phenoxyphenyldiphenylethylsilane) (ml/g)	—	1337

An obvious application of a stationary phase with such a high content of aromatic groups is the separation of polynuclear aromatic compounds. Fig. 2 shows the temperature-programmed analysis of a known mixture of components with a wide boiling range together with three alkanes on MPHT.

Another interesting application is the separation of drug mixtures, and a chromatogram illustrating the resolution of several barbiturates is presented in Fig. 3. While barbiturates are liable to produce peaks with significant tails on many stationary phases, the present results show very good peak symmetry even for components with relatively long retention times.

Finally, the utilization of the good high-temperature properties of MPHT is demonstrated by the separation of low-molecular-weight poly(*m*-phenyl ethers).



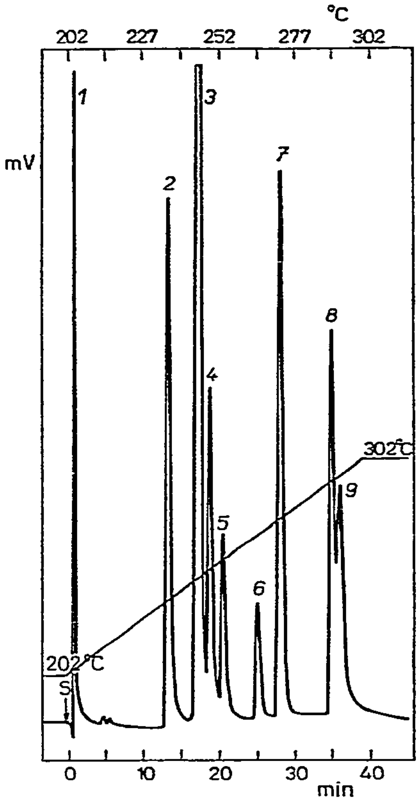


Fig. 2. Separation of high-boiling hydrocarbons. Conditions as in Fig. 1, except 20% MPHT and column temperature programmed from 184 to 284°C at 4°C/min, then isothermal for 40 min. Peaks: 1 = solvent; 2 = eicosane; 3 = fluorene; 4 = docosane; 5 = pyrene; 6 = 2-methylanthracene, hexacosane, 1-methylpheranthrene; 7 = 2-phenylnaphthalene; 8 = fluoranthene; 9 = 9,10-dimethylanthracene; 10 = 11H-benzo[*b*]fluorene; 11 = 1,2-benzanthracene.

Fig. 3. Separation of barbiturates. Conditions as in Fig. 2 except column temperature programmed from 202 to 302°C at 2.5°C/min. Peaks: 1 = methanol; 2 = barbital; 3 = allobarbital, diallylbarbital, aprobarbital; 4 = amobarbital; 5 = pentobarbital; 6 = phenobarbital; 7 = hexobarbital; 8 = eudan; 9 = thiopentobarbital.

These compounds are commercially important as, *e.g.*, diffusion pump fluids and gas chromatographic stationary phases, etc. Fig. 4 shows the separation of such material, which consists of the five-ring oligomer and probably its four- and six-ring analogues.It is worth noting that the elution takes place at considerably low temperatures with regard to the boiling points of the components being analysed, without loss of sharpness of the peaks. For the five-ring component the difference between the operating temperature and the boiling point is 234°C and for the six-ring analogue it is 275°C.

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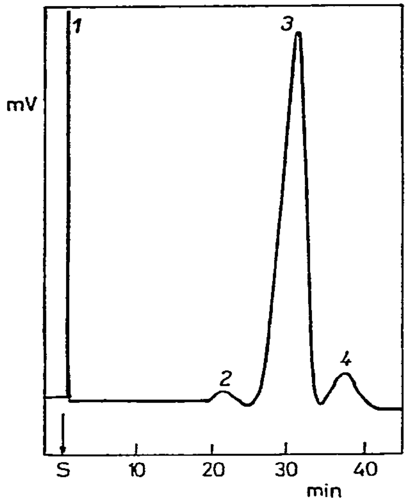

Fig. 4. Separation of a poly(phenyl ether) mixture. Conditions as in Fig. 1 except column temperature, 321 °C. Peaks: 1 = solvent; 2 = 1-phenyloxy-3-(3-phenyloxyphenyloxy)benzene (b.p. 463 °C/760 Torr[12]); 3 = 1,3-bis-(3-phenyloxyphenyloxy)benzene (b.p. 555 °C/760 Torr[12]); 4 = 1-(3-phenyloxyphenyloxy)-3-tris-(3-phenyloxyphenyloxy)benzene (b.p. 596 °C/760 Torr[12]).

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