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## Note

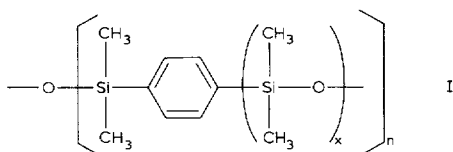
### Use of poly(silarylene-methylphenylsiloxane) block copolymer as a thermostable stationary phase in capillary column gas chromatography

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It is known that silicone polymers containing silarylene links possess relatively high thermal stability<sup>1-5</sup>. The structure of these polymers is



where  $x = 1-4$ . The polymer where  $x = 1$  is the most thermostable<sup>1</sup>.

Yudina *et al.*<sup>6</sup> described packed column gas chromatography (GC) performed on a stationary phase synthesized by copolymerization of 1,4-bis(hydroxydimethylsilyl)benzene and trifluoropropylsilane; the authors claimed that the maximum working temperature was raised tremendously compared with corresponding non-arylene-silicones. There are indications that polymers containing diphenylene, naphthalene and diphenyl oxide bridges in the chain are even more stable<sup>2,3,7</sup>. The thermal stability and degradation behaviours of silarylene-siloxane polymers have recently been described<sup>8</sup>. Furthermore, the preparation of silarylene copolymers with different functional groups has been reported<sup>9-11</sup>.

This paper presents the preparation of a block copolymer, poly(arylene-methylphenyl)siloxane, and the *in situ* immobilization of the phase with dicumyl peroxide or ozone. Columns prepared with this stationary phase could routinely be used at temperatures up to 360°C.

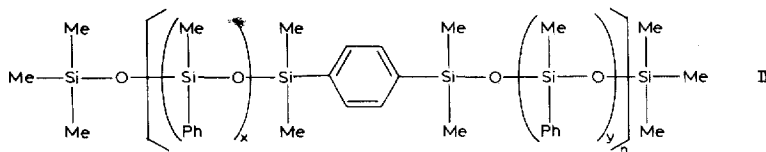
## EXPERIMENTAL

### Preparation of poly(arylene-methylphenylsilicone) (aryl-Me-Ph)

A copolymerization was performed of 0.02 mol methyl(phenyl)dichlorosilane (Me-Ph-sil) and 0.01 mol 1,4-bis(hydroxydimethylsilyl)benzene (silarylene); both chemicals were obtained from Petrarch Systems Inc. (Bristol, PA, U.S.A.). The Me-Ph-sil was refluxed in an excess of dry methanol until evolution of HCl gas ceased.

The resulting methoxy-ether was then cooled and mixed with the silarylene, dissolved in methanol. Distilled water, 0.1 mol, was added to this mixture and refluxed for 6 h. The oily product (aryl-Me-Ph) was dissolved in *ca.* 25 ml dichloromethane and separated from the water-methanol phase. After washing ten times with *ca.* 25 ml distilled water, the solvent was evaporated from the aryl-Me-Ph product. For further polymerization of the aryl-Me-Ph polymer, 0.1% (w/w) of tetramethylammonium hydroxide (Aldrich, Milwaukee, WI, U.S.A.) in methanol was added at 25°C. Whilst stirring, the temperature was increased to 115°C (*ca.* 5°C/min); nitrogen, 10 ml/min, was blown over the aryl-Me-Ph product to prevent oxidation. After 2 h at 115°C a gum-like product was formed. The temperature was then quickly increased to 150°C and maintained for 5 min to destroy the catalyst. The polymer was dissolved in 25 ml toluene and end-capped with trimethylchlorosilane by refluxing the mixture for 12 h. The silicone was washed five times with distilled water, whereafter the toluene was evaporated. The resulting siloxane was mixed with 25 ml of methanol-dichloromethane (2:1) to remove the by-products of the catalyst and low-molecular-weight polymer; this was repeated five times. The solvent was then evaporated under reduced pressure. The product was freeze-dried overnight; no water content could be detected by infra-red spectroscopy.

The aryl-Me-Ph gum thus formed may have the following composition:



#### Deactivation and coating

Fused-silica capillaries were flushed with dry nitrogen for 2 h at room temperature, after which they were dynamically coated with the deactivation solution, a 3% (v/v) methyl(phenyl)cyclosiloxane in toluene, as described previously<sup>12</sup>.

The capillaries were coated statically with (a) a 0.5% (w/v) solution of the stationary phase in dichloromethane containing dicumyl peroxide (DCP) (0.5%, w/v of the stationary phase content). (b) a 0.5% (w/v) solution of the stationary phase in dichloromethane or (c) (for untreated nitrogen-flushed fused-silica capillaries) with a 0.5% solution as in (b) plus decamethylcyclopentasiloxane (D<sub>5</sub>) (Petrarch), 2% of the stationary phase content.

After the coating procedure, the columns were flushed for 3–4 h with nitrogen. Columns coated according to (a) were then sealed in a flame and heated at a rate of 15°C/min to 180°C, then isothermally for 3 min, cooled and rinsed with 10 ml of dichloromethane. Columns coated according to (b) were filled at room temperature with ozone by suction of an ozone-oxygen mixture for 15 min as described earlier<sup>12,13</sup>, flushed with nitrogen for 3 h and rinsed with 10 ml dichloromethane. Columns coated according to (c) were sealed in a flame, heated at a rate of 5°C/min to 350°C and maintained at this temperature for 2 h (the deactivation step). The columns were flushed with nitrogen at 150°C for 1 h to remove excess of D<sub>5</sub>, after which they were filled with ozone at room temperature for 15 min, flushed with

nitrogen for 3 h and rinsed with dichloromethane. After rinsing, the columns were conditioned at 330°C for 10 h, programmed at a rate of 3°C/min.

The columns were tested in a Hewlett-Packard gas chromatograph, Model 5790. Hydrogen was used as carrier gas (50 cm/min), and the detector was a flame ionization detector. The fused-silica capillaries, 0.22 mm I.D., were purchased from Chrompack (Middelburg, The Netherlands).

## RESULTS

It has been shown that 1,4-bis(hydroxydimethylsilyl)benzene incorporated in a polymer will stabilize the silicone polymer<sup>6</sup>; bleeding decreased significantly and the maximum allowable operating temperature (MAOT) increased<sup>6</sup>.

Incorporation of such arylene units in the main chain can produce polymers with a very high thermal stability<sup>14,15</sup>. This is explained by the greater difficulty, in this case, of breaking silicon-carbon bonds than of breaking silicon-oxygen bonds<sup>4</sup>. For a poly(methylphenylsiloxane), in an inert atmosphere, scission of the Si-O bond is followed by the formation of different cyclic structures. However, the introduction of rigid phenylene units into such a chain retards or prevents the formation of cyclic structures and therefore stabilizes the molecule<sup>8</sup>. Furthermore, the thermal stability increases with increasing phenyl content, see Table I. The structure of the aryl-Me-Ph molecules presented in Table I is:

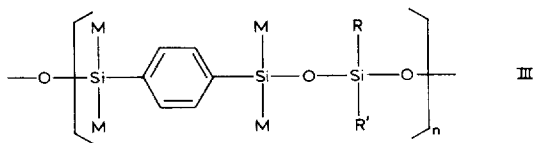


TABLE I

THERMAL GRAVIMETRIC ANALYSIS DATA FOR SOME SILICONES IN NITROGEN, FROM REF. 15

A = Poly(dimethylsiloxane); B, C, D = arylene-siloxane block copolymers.

Polymer	Weight loss		Structure III	
	10%	20%	R	R'
A	355°C	390°C		
B	380°C	420°C	Me	Me
C	410°C	460°C	Me	Ph
D	445°C	490°C	Ph	Ph

The poly(arylene-methylphenylsiloxane) was very suitable for the use as a stationary phase, Fig. 1. Highly efficient columns could thus be prepared, with an HETP of 0.22 mm for naphthalene at 90°C; this corresponds to a coating efficiency of 102%. The Kováts indices for *n*-octanol and naphthalene at 90°C were 1133 and 1299 respectively. Column bleeding was very low even at 360°C. Columns coated with this stationary phase could successfully be used for the analysis of diglycerides, Fig. 2.

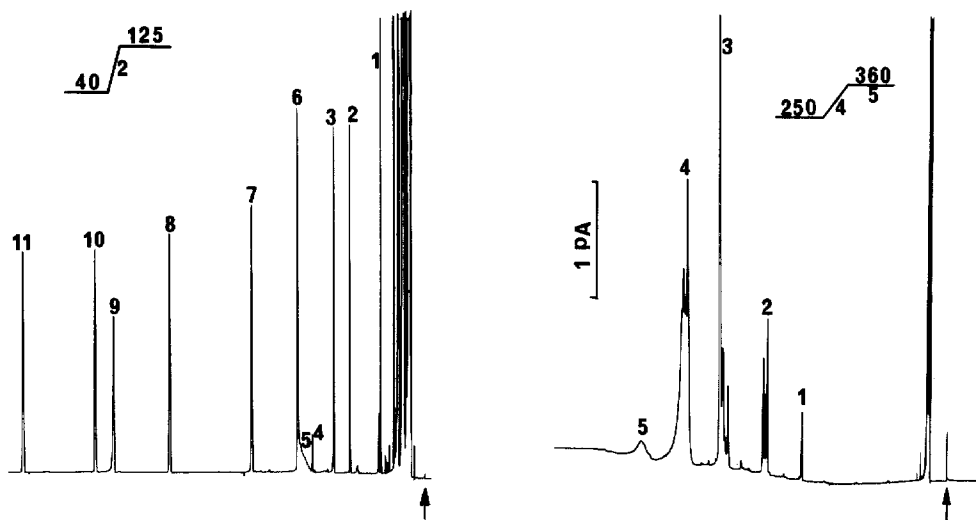


Fig. 1. Gas chromatogram of Grob's test mixture run on a fused-silica column (10 m  $\times$  0.22 mm I.D.),  $d_f$  = 0.25  $\mu$ m. Peaks: 1 = decane; 2 = undecane; 3 = *n*-octanol; 4 = *n*-nonanal; 5 = 2-ethylhexanoic acid; 6 = 2,6-dimethylphenol; 7 = 2,6-dimethylaniline; 8, 10, 11 = C<sub>10</sub>, C<sub>11</sub>, C<sub>12</sub> fatty acid methyl esters; 9 = dicyclohexylamine.

Fig. 2. Gas chromatogram of trimethylsilyl-derivatized diglycerides on a fused-silica column (10 m  $\times$  0.22 mm I.D.),  $d_f$  = 0.15  $\mu$ m. Peaks: 1 = C<sub>32</sub>; 2 = C<sub>34</sub>; 3 = C<sub>36</sub>; 4 = C<sub>38</sub>; 5 = C<sub>40</sub> (total carbon numbers of the fatty acids are given).

Moreover, the phase was suitable for the separation of column-bleed products from immobilized Carbowax and for cyanopropyl(tolyl)cyclosiloxanes<sup>16</sup>. Furthermore, a silarylene-siloxane copolymer having 33% cyanopropyl substituents was stable up to 300°C<sup>17</sup>.

It was found by Lipsky and McMurray<sup>18</sup> that the acidity of some batches of fused-silica capillary tubings could be diminished by flushing with nitrogen before use. Thus before the different procedures we flushed the capillaries with nitrogen for 30 min at 150°C to remove acidic volatile compounds. It was found that, from a particular batch of fused-silica capillaries, after purging with nitrogen (10 ml/min) for 2 h at room temperature in 10 ml of deionized water, 2.3  $\mu$ g Cl<sup>-</sup> and 3.7  $\mu$ g NO<sub>3</sub><sup>-</sup> per 50 m could be detected by ion-exchange chromatography. After further rinsing of the column with 10 ml of deionized water no anions could be detected.

## CONCLUSION

Block copolymer siloxanes with silarylene links incorporated exhibit high thermal stability. Columns coated with poly(arylene-methylphenylsiloxane) could be used at temperatures up to 360°C. Silicone stationary phases with well defined silarylene links will be described elsewhere.

## ACKNOWLEDGEMENTS

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