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IN SITU GUMMIFICATION OF METHYLPHENYLSILICONES IN FUSED-SILICA CAPILLARY COLUMNS

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SUMMARY

A technique is described for obtaining immobilized coatings of methylphenylsilicones in fused-silica capillaries. The columns are statically coated with a very viscous methylphenylsilicone polymer which is terminated with silanol functions. Gummification in the column is carried out by heat-curing. An immobilized and solvent-resistant methylphenylsilicone film is then obtained without the need for addition of peroxides.

INTRODUCTION

Much effort is currently being directed at the preparation of fused-silica columns with immobilized films of polar polysiloxanes. Because of their high polarity and unique selectivity, the phases most interesting to investigate are the methylphenylsilicones with a high phenyl content (OV-17, OV-22, OV-25), the cyanopropylsilicones (Silar 10C, OV-275) and the methyltrifluorosilicones (QF-1, OV-210). The availability of efficient, inert and thermally stable columns with these phases will further broaden the applicability of capillary gas chromatography (GC), but, only if it is possible to manufacture the columns reproducibly with well defined polarity and selectivity. This last point is very important, because in order to make high-quality columns, capillary-compatible stationary phases have to be synthesized. In practice, this means that the above phases must be synthesized in gum form. Moreover, the phases should preferably be immobilized. These two requirements can be met in different ways, but each leads to a slightly different polarity or selectivity.

Although limited success has been reported with liquid methylphenylsilicones coated on fused-silica walls[1,2], the synthesis of high-molecular-weight linear methylphenylsilicones that can eventually be converted from the highly viscous state into the elastic, insoluble state by cross-linking, is necessary. The effect of the viscosity of methylphenylsilicones on film stability in capillary columns has recently been studied by Wright *et al.*[3]. Methylphenylsilicones with a gum character have been synthesized by Buijten *et al.*[4] and Peaden *et al.*[5]. Buijten *et al.* polymerized a prepolymer, obtained by alkaline hydrolysis of methylphenyldichlorosilane, using sodium trimethylsilanolate as catalyst. The product was end-capped with trimethylchlorosilane. The phase was evaluated by us and showed excellent properties for capillary gas

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chromatography. As expected, the phase could not be immobilized by adding peroxides. Cross-linking of pure methylphenylsilicones with a high phenyl content has been found to be particularly difficult. Recently, immobilization was achieved by the same group by incorporating 3.3% of vinyl groups in the phenylmethylsilicone matrix or by replacing phenyl by tolyl groups[6]. Cross-linking was performed with concentrations of 3 and 1% dicumyl peroxide, respectively. Wright *et al.* converted the chlorosilanes into the hydroxysilanes, and polymerization was accomplished by adding 0.05% of tetramethylammonium hydroxide and heating at 130°C.

Trimethylchlorosilane was added to destroy the catalyst and to end-cap the polymer. The high-molecular-weight material was obtained by precipitation from dichloromethane–methanol. Efficient immobilization could be achieved by incorporating vinyl groups in the silicone matrix.

It is obvious, however, that the introduction of vinyl or tolyl groups to replace phenyl groups will necessarily affect the polarity and selectivity of the phases. Strict comparison of results, *e.g.*, with OV-17, therefore becomes difficult. During our investigations on the synthesis of methylphenylsilicone gums by alkaline hydrolysis we have observed that insoluble gums are obtained by heat-curing at elevated temperatures of unterminated methylphenylsilicone (the end functions are silanol groups).

This prompted us to coat capillary columns with such very viscous prepolymers and to continue the polymerization or gummification of the living polymer into the column by heat-curing. This paper describes the first results obtained with this approach to immobilization. Living polymers have also been used by Madani and Chambaz[7] to obtain chemically bonded methylphenylsiloxane films.

EXPERIMENTAL

A silicone similar in composition to OV-17 was synthesized from methylphenyldichlorosilane by alkaline hydrolysis. This liquid silicone, called prepolymer 1, was used to deactivate the fused-silica columns. The capillaries were previously leached with hydrochloric acid at 350°C. Deactivation was obtained by dynamically coating the columns with a 0.3% solution of the prepolymer in dichloromethane at a rate of 2 cm/sec. The capillaries were then evacuated, sealed, heated to 300°C at 3°C/min and then held isothermally at 300°C for 15 h. Excess of reagent was removed by rinsing the columns with 10 ml of dichloromethane. Prepolymer 1 was further polymerized to a semi-gum, called prepolymer 2, by heat-curing under nitrogen. The viscosity of the phase was continuously controlled to avoid complete gummification. The pretreated capillaries were then statically coated with a 0.1–0.3% (w/w) solution of prepolymer 2 in dichloromethane. The silanol-terminated prepolymer 2, coated on the column wall, was immobilized by *in situ* gummification by heat-curing. This was achieved by heating the column repeatedly from 150 to 250°C at 3°C/min for 15 h under a low flow of carrier gas (0.1 ml/min).

RESULTS AND DISCUSSION

The gummification of methylphenylsilicone prepolymer 2 in the column is illustrated in Fig. 1. A 10 m × 0.32 mm I.D. fused- silica column was coated with the highly viscous prepolymer 2, which is still soluble in dichloromethane. After heat-

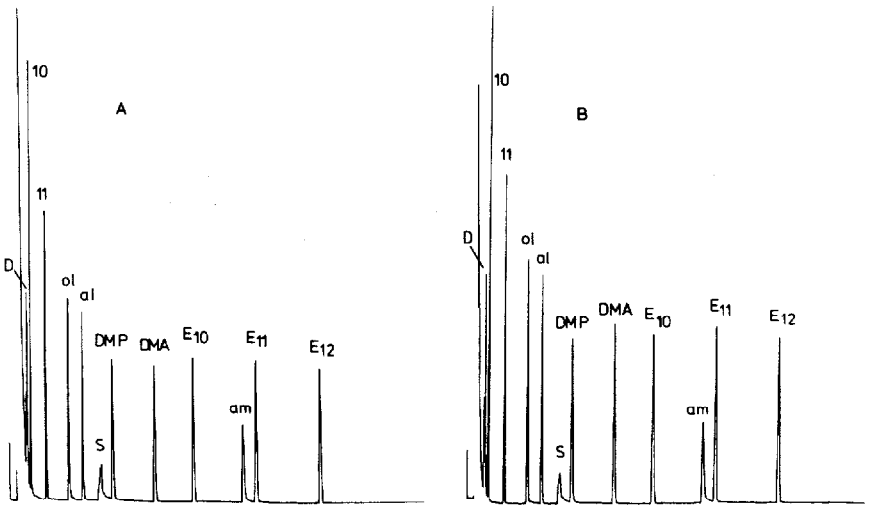

Fig. 1. Chromatogram obtained with a 10 m × 0.32 mm I.D. column, temperature-programmed from 60 to 130°C at 3°C/min, (A) before rinsing and (B) after rinsing with 5 ml of dichloromethane. Test mixture according to Grob. D = 2,3-Butanediol; 10 = *n*-decane; 11 = *n*-undecane; ol = octanol-1; al = nonanal; S = 2-ethylhexanoic acid; DMP = 2,6-dimethylphenol; DMA = 2,6-dimethylaniline; E10 = decanoic acid methyl ester; am = dicyclohexylamine; E11 = undecanoic acid methyl ester; E12 = dodecanoic acid methyl ester.

curing, Grob's polarity mixture was analysed in a temperature-programmed run from 60 to 130°C at 3°C/min (Fig. 1A). The inertness was indicated by elution of all the compounds injected in the 3-ng range. The column was then rinsed with 5 ml of dichloromethane and re-installed in the GC apparatus. Fig. 1B reveals that this treatment did not affect the performance of the column. The elution temperature of the C_{12} acid methyl ester is 114°C in both cases or, in other words, the yield of immobilization is 100%. The immobilized film shows a chromatographic efficiency* of above 80% and thermal stability to at least 300°C.

The procedure described offers the advantage that no groups other than methyl and phenyl are present in the polymer finally deposited on the column wall. Therefore, the polarity and selectivity are well defined and equal to that of OV-17. The gum phase is terminated by silanol groups, which can be capped by flushing the column with a silylating agent in toluene or by injecting hexamethyldisilazane at elevated temperatures. The insolubility is due only to the very long chain of the polymer. However, when required, cross-linking can be obtained by adding a trialkoxysilane to the prepolymer gum. Cross-linking condensation takes place with the elimination of alcohol. This will not affect the polarity of the phase and the activity of the column, as in the case of the addition of peroxides and/or the incorporation of vinyl or tolyl groups in the polymer.

The heat-curing conditions are currently being further optimized, and different

* We suggest replacing the term *coating efficiency* (proposed by us) by the term *chromatographic efficiency* (CE value).

batches are being evaluated by spectroscopic techniques, thermogravimetric analysis and gel-permeation chromatography.

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