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Silicone gum of OV-225 type for open-tubular gas chromatography

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Abstract

A silanol-terminated silicone having 25% cyanopropyl, 50% methyl and 25% phenyl substitution was prepared and a method for its immobilization in open-tubular columns was developed. This stationary phase showed good thermal stability at temperatures up to 300°C, and it was immobilized to 80% by means of thermal treatment. Its selectivity was excellent for the separation of azaarenes.

1. Introduction

Silicones are by far the most widely applied type of stationary phases for gas chromatography (GC). The properties of silicone stationary phases can be varied by the use of different types of substituent groups on the silicone backbone. Polysiloxanes containing at least two different selectively acting substituent groups constitute an important class of medium-polarity stationary phases. These phases provide a relatively broad range of selectivities that could be useful for the separation of samples containing different classes of organic compounds. In recent years, a relatively large number of phases belonging to this group have been developed, such as methoxyphenylpolysiloxanes [1], cyanophenylpolysiloxanes [2], nitrophenyl- and nitromethoxyphenyl-

polysiloxanes [3] and a cyanobiphenylpolysiloxane [4].

In the development of new stationary phases for open-tubular GC, it may be advantageous to consider the extensive experience concerning stationary phase selectivity that was obtained during the packed column era [5–7]. The silicone OV-225, which contains 25% cyanopropyl, 50% methyl and 25% phenyl substitution, was one of the more useful moderately polar stationary phases at that time. The application of this phase to open-tubular columns has, however, been less successful. In the original version OV-225 is an oil, and physically stable films cannot be created in open-tubular columns with this polymer. In order to provide possibilities for immobilization in open-tubular columns, two more recent versions of OV-225 have been made commercially available by Ohio Valley Specialty Chemical (Marietta, OH, USA). These were a vinyl-terminated version intended for immobilization by means of radical initiators and a silanol-terminated version intended for thermal immobiliza-

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tion. The viscosity of these polymers was low, however.

The silanol-terminated polymer OV-225-OH (Ohio Valley) was applied to open-tubular glass columns by Blum *et al.* [8]. A trifunctional cross-linking reagent, cyanopropyltriethoxysilane, was added to the coating solution in order to facilitate immobilization, and thermal stability up to 390°C was claimed. The degree of immobilization was not given. The vinylated OV-225 has been immobilized in fused-silica [9] and glass columns [10] by means of dicumyl peroxide-initiated cross-linking. The maximum operation temperature of the columns was 250°C.

The aim of this work was to develop an immobilizable, thermally stable version of the classical polymer OV-225. Two polymers, having the same gross composition but with different arrangements of the substituent groups, were synthesized. The chromatographic properties of the polymers were demonstrated. One of the polymers showed good thermal stability and immobilizability.

2. Experimental

Three types of silanol-terminated silicones of the OV-225 type have been evaluated for use as stationary phases. Two of these were synthesized in our laboratories; polymer 1 was composed of cyanopropyl–methyl and phenyl–methyl units, and in polymer 2 the basic unit consisted of one bis(cyanopropyl), one diphenyl and two dimethyl groups. The third polymer was the commercially available OV-225-OH. Polymer 1 was synthesized by cohydrolysis of dimethoxydiphenyldimethyldisiloxane and dimethoxymethylcyanopropylsilane in appropriate amounts followed by polymerization at 100°C using tetramethylammonium hydroxide (TMAH) as catalyst. Polymer 2 was synthesized by cohydrolysis of dimethoxydiphenyltetramethyltrisiloxane and bis(cyanopropyl)dimethoxysilane in appropriate amounts. Polymerization was performed as for polymer 1.

Fused-silica capillary tubing of I.D. 0.25 μm (Chrompack, Middelburg, Netherlands) was used as the column material in lengths of 10 m.

Before coating, some capillaries were treated with HCl and dehydrated as described previously [11]. A few capillaries were deactivated by heat treatment at 280°C with a silicone oil of the same composition as polymer 1.

For coating, the stationary phase was dissolved in dichloromethane in appropriate concentrations and a trifunctional cross-linking reagent, cyanopropyltrimethoxysilane, was added to the coating solution. All columns were coated by the static method at room temperature. After coating, the columns were closed and heated at 60°C for 1 h as recommended by Blum [12] when using tetramethoxydimethyldisiloxane as a cross-linking reagent.

2.1. Column evaluation and stationary phase immobilization

The GC columns were evaluated on a Carlo Erba HRGC 5300 Mega system connected to a laboratory data system (ELDS; Chromatography Data Systems, Kungshög, Sweden). A polarity mixture was injected at 100°C, and a test mixture containing *n*-alkanes and biphenyl was injected at a column temperature of 125°C. Hydrogen at a rate of 50 cm/s was used as the mobile phase, and the injector splitting ratio was 1:100. The injector temperature was 280°C and the detector temperature was 300°C. For column bleeding tests at temperatures above 300°C, the detector temperature was set to the maximum column temperature.

A first test was performed after heating at a rate of 1°C/min to 100°C and maintaining this temperature for 1 h. The second test was performed after heating to 280°C at a rate of 0.5°C/min, and maintaining this temperature for 10 h. A third test was performed after rinsing of the column with 5 ml of dichloromethane. Column bleeding was evaluated in temperature-programmed runs at 5°C/min.

3. Results and discussion

The commercial phase OV-225-OH is a low-viscosity silicone oil. Polymer 1 was a gum, but polymer 2 could not be polymerized to a true

gum when TMAH was used as a catalyst. In order to obtain the highest possible molecular mass, equilibration with TMAH was interrupted when the viscosity of the polymer was at a maximum. A highly viscous oil was obtained.

Silanol-terminated polymers were used in this work. It has been established that, for phenyl-containing silicones, silanol termination results in better thermal stability than trimethylsiloxy termination [13–15]. Further, end-capping of a polysiloxane by means of a chlorosilane involves the formation of HCl, which can attack the cyano groups.

3.1. Stationary phase immobilization

Immobilization of polymer 1 was first attempted by heating without a cross-linker. No immobilization was achieved after such a treatment. With the addition of a cross-linker, the stationary phases could be immobilized, but only when coated on HCl-treated surfaces. Immobilization therefore could not be achieved when using untreated fused silica (H_2 flushed), deactivated fused silica or fused silica that had been HCl treated and deactivated. Clearly, surface silanol groups are necessary for the immobilization. The importance of condensation between terminal OH groups on the stationary phase and surface silanols for the immobilization has been emphasised by Blum and co-workers [16,17].

The highest degree of immobilization was achieved with 2% of the cross-linking reagent (Table 1). Polymer 2 was immobilized to a much lower extent than polymer 1 (Table 1). It seems that the combination of bis(cyanopropyl) and diphenyl groups makes immobilization more difficult. Immobilization of the commercial OV-225-OH was not successful (Table 1).

The addition of trimethoxycyanopropylsilane to the stationary phase alters the surface tension. Deactivated fused silica was therefore not wetted when 1% or more of this cross-linker has been added to the phase, and the wettability of HCl-treated fused silica was lost when 4% of cross-linker was added to the stationary phase.

The mechanisms active in the immobilization of polymers of OV-225-OH composition are different from those active in the immobilization

Table 1
Influence of percentage of cross-linker and type of polymer on immobilization

Polymer	Cross-linker (%)	Polymer immobilization (%)
Polymer 1	0.5	30
	1	61
	2	79
	3	66
	4	— ^a
Polymer 2	2	5
OV-225-OH	2	0

^a The stationary phase does not wet the support.

of the silanol-terminated phenyl-containing silicones investigated previously, Sila 1 [11], OV-61-OH and Sila 3 [18] and OV-17-OH [19]. These polymers have high thermal stabilities, and immobilization could be attempted at 370°C. At this temperature, phenyl groups in silanol-terminated polysiloxanes are cleaved off and branched structures are formed [13,20]. It was concluded that such a cleavage of phenyl groups contributed strongly to the relatively high degree of immobilization that was achieved with these polymers [11,18,19]. Neither HCl treatment of the supporting fused silica nor the addition of a trifunctional cross-linker was found necessary for the immobilization of these polymers. As a consequence of the destabilizing effect of the cyanopropyl groups, polymers of the OV-225 type could not be heated to the high temperatures applied for phenylsilicones. Immobilization was therefore attempted by the addition of a reagent that promoted cross-linking and surface bonding.

3.2. Column adsorptive activity

Columns where polymer 2 had been coated on untreated fused silica showed relatively good deactivation (Fig. 1A). Coating Polymers 1 and 2 on HCl-treated capillaries resulted in acidic columns; nicotine was not eluted (Fig. 1B). Conditioning at 280°C resulted in an improved elution of nicotine (Fig. 1C).

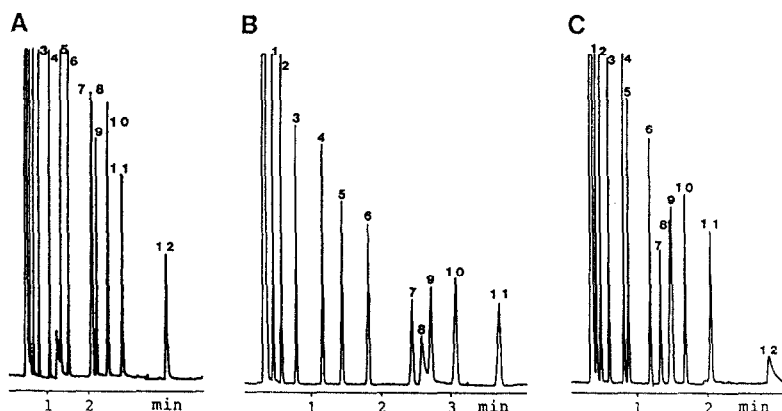


Fig. 1. Gas chromatograms (flame ionization detection) of a polarity mixture on capillary columns of dimensions 10 m \times 0.25 mm I.D. Columns: (A) untreated fused silica coated with polymer 2 and 2% of cross-linker; (B) HCl-treated fused silica coated with polymer 1 and 2% of cross-linker; (C) same column as in (B), but after thermal treatment for 10 h at 280°C. Film thickness: (A and B) 0.15 μ m; (C) 0.13 μ m. Conditions: split injection; isothermal at 100°C. In (A) and (B) the columns were tested after conditioning for 1 h at 100°C. Peaks: 1 = *n*-undecane; 2 = *n*-dodecane; 3 = *n*-tridecane; 4 = *n*-tetradecane; 5 = aniline; 6 = *n*-pentadecane; 7 = phenol; 8 = decanol; 9 = 2,6-dimethylphenol; 10 = 2,6-dimethylaniline; 11 = 2-methylnaphthalene; 12 = nicotine. Sample amount, *ca.* 1 ng of each substance.

3.3. Column polarity and thermal stability

The commercial OV-225-OH showed a lower polarity than polymers 1 and 2 (Table 2). Further, the film thickness and the polarity of

columns coated with OV-225-OH decreased drastically on conditioning. Also, the commercially available OV-225 gives a lower Kováts retention index for biphenyl than the polymers that were synthesized for this work. A value of

Table 2

Properties of open-tubular columns (10 m \times 0.25 mm I.D.) coated with silicones of the OV-225 type with an original film thickness of 0.15 μ m

Column No.	Stationary phase	Cross-linker (%)	Column treatment ^a	<i>k'</i> (100°C)		HETP (100°C)		Kováts index		
				2-Me-naphthalene	C ₁₅	2-Me-naphthalene	C ₁₅	2-Me-naphthalene (100°C)	Decanol (100°C)	Biphenyl (125°C)
1	OV-225-OH	2	A	11.6	5.8	1.71	0.59	1614	1560	1737
			B	7.2	3.0	0.56	0.91	—	1533	1706
2	Polymer 1	2	A	10.1	4.5	0.27	0.43	1639	1573	1773
			B	8.6	3.9	0.30	0.41	1637	1568	1769
			C	6.7	3.1	0.30	0.40	1634	1567	1767
3	Polymer 1	3	A	10.3	4.6	0.30	0.40	1639	1572	1773
			B	7.9	3.6	0.30	0.39	1634	1563	1765
			C	5.1	2.4	0.30	0.36	1629	1564	1761
4	Polymer 2	2	A	9.6	4.0	0.30	0.49	1655	1588	1792
			B	8.5	3.7	0.25	0.32	1646	1580	1782

^a A = Conditioned at 100°C; B = programmed at 0.5°C/min to 280°C, isothermal for 10 h; C = after extraction with methylene chloride.

1748 at 120°C has been reported for OV-225 [2], whereas polymer 1, without crosslinker, gave 1756 at that temperature. Further, the polymer containing diphenyl and bis(cyanopropyl) units (polymer 2) showed a higher polarity than the cyanopropyl–methyl, methyl–phenyl polymer (polymer 1). The retention index for biphenyl at 125°C on polymer 1 (2% of cross-linker) was thus 1773 and on polymer 2 (2% of cross-linker) it was 1792. On the other hand, silicones of the OV-17 type showed a higher polarity when composed of methyl–phenyl units than when composed of diphenyl and dimethyl units [19]. It therefore seems that biscyanopropyl units result in higher polarities than cyanopropyl–methyl units for the polymer gross composition investigated in this work.

Columns coated with polymer 1 showed higher thermal stabilities than columns coated with polymer 2 (Table 3). The capacity factor of biphenyl on polymer 1 was thus 88% of the original after conditioning for 10 h at 280°C, whereas 56% remained after such a treatment of columns coated with Polymer 2. Polymer 1 was, however, fairly stable up to 300°C (Table 3). After conditioning of polymer 2-coated columns at 300°C for 10 h, the capacity factor of biphenyl was only 25% of its original value. In general, diphenyl substituents increase the thermal stability of a silicone [19,21], and polymer 2 was

expected to show the highest thermal stability. The relatively low thermal stability of polymer 2 could be explained by two factors: it had a relatively low molecular mass and it could not be immobilized.

3.4. Separation of azaarenes

The separation of a test mixture of azaarenes has been extensively investigated [1–4,18,22,23]. Complete separation of the mixture was obtained on polymer 1 under isothermal conditions with a column of dimensions 10 m × 0.25 mm I.D. (Fig. 2). Peaks 3 and 4 in Fig. 2 are the most difficult to separate in the test mixture; they have been separated on 20 m × 0.31 mm I.D. columns coated with highly polar phases having 75 or 88% cyano substitution [22,23]. However, separation was achieved also on a trimethoxyphenyl- [1], a cyanophenyl- [2] and a nitromethoxyphenyl-substituted polysiloxane [3]. The separations were here obtained on narrower columns of 0.20 mm I.D. The length of the trimethoxyphenyl- and nitromethoxyphenylsilicone-coated columns were 10.5 or 10 m, the number of theoretical plates, N , on these columns being 41 000–44 000; the separation on the cyanophenylsilicone-coated column was achieved on a 20-m capillary with $N = 82 000$. The separation in Fig. 2 was obtained on a

Table 3
Column properties after conditioning

Thermal treatment	Polymer 1			Polymer 2		
	k' (biphenyl)	Phase content (%)	Kováts index (biphenyl) (125°C)	k' (biphenyl)	Phase content (%)	Kováts index (biphenyl) (125°C)
Short conditioning	6.1	100	1773	5.6	100	1790
280°C, 10 h	5.3	88	1769	3.1	56	1774
After extraction	4.1	67	1767	–	–	–
300°C, 10 h	3.4	56	1763	1.4	25	1733
320°C, 10 h	2.8	46	1757			
340°C, 10 h	2.3	38	1746			
360°C, 10 h	1.3	21	1723			
380°C, 10 h	1.0	16	1702			

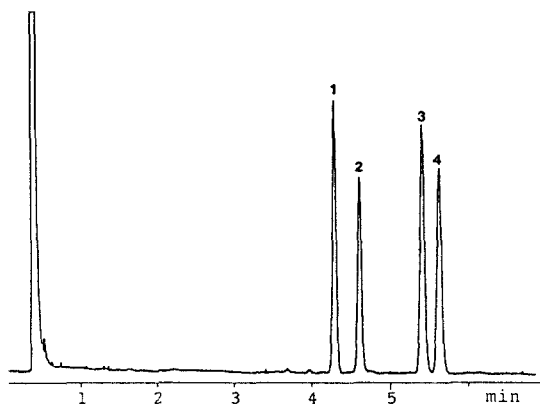


Fig. 2. Gas chromatogram (flame ionization detection) of azaarenes. Column as in Fig. 1B. Conditions: split injection; isothermal at 160°C. Peaks: 1 = 7,8-benzoquinoline; 2 = acridine; 3 = phenanthridine; 4 = 5,6-benzoquinoline.

column having larger I.D. and the plate count was accordingly lower, $N \approx 33\,000$ plates. In spite of this, the separation was better than previously published, illustrating the excellent selectivity that can be achieved with polymer 1. Further, the time of analysis was *ca.* 22 min in refs. 2 and 3 and 17 min in ref. 1, whereas in this work (Fig. 2) the time of analysis was below 6 min.

The polarities of the trimethoxyphenyl- and nitromethoxyphenyl-substituted polymers, as expressed by the Kováts retention index of biphenyl [1,3], were in the same range as for polymer 1, whereas the polarity of the cyanophenyl-substituted polysiloxane was lower [2]. The thermal stabilities of the trimethoxyphenyl- and the cyanophenyl-substituted silicones and polymer 1 were in the same range, 280–300°C. The nitromethoxyphenyl phase was stable only up to 230°C.

In conclusion, polymer 1 showed acceptable thermal stability up to 300°C. After addition of a cross-linking reagent, the phase could be immobilized to 80% by means of thermal treatment. Excellent separation of azaarenes was demonstrated. Although several new stationary phases, intended for the same purpose in GC as OV-225, have been reported, the classical OV-

225 type of phase still provides an attractive alternative.

Acknowledgements

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