

CHROM. 15,448

GAS CHROMATOGRAPHIC STUDY OF CHEMICALLY BONDED POLY-METALLOPHENYLSILOXANES

W. WASIAK and W. SZCZEPANIAK*

Faculty of Chemistry, A. Mickiewicz University, 60-780 Poznań (Poland)

(First received April 14th, 1982; revised manuscript received October 6th, 1982)

SUMMARY

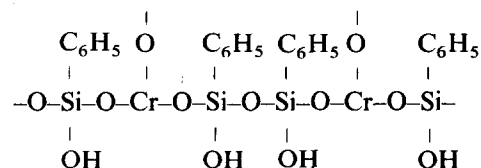
The synthesis of a series of polymetallophenylsiloxanes containing atoms of Cu, Mg, Cr, La and Nd has been carried out. The polymers were examined by means of gas chromatography after they had been chemically bonded to a silica surface. The copper- and chromium-containing polymers show considerably higher affinity toward olefins than the other polymers.

INTRODUCTION

Most stationary phases commonly used in gas chromatography (GC) are comprised of polysiloxanes. Two review papers by Haken^{1,2} give a clear idea of the development potential of such phases which possess thermal and chemical stability, low volatility, high selectivity and availability and are readily modified.

Similar qualities are exhibited by another group of silicon compounds, namely polymetalloorganosiloxanes. The principal structural difference between these two groups of compounds is that polymetalloorganosiloxanes possess divalent or higher

valent metal atoms in the siloxane chain $-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-$. As a result, polymers of linear or cyclic structures are formed³:



The molecular weight of such a polymer depends on the synthesis conditions, the amount of incorporated metal, etc.

The introduction of a new function (*i.e.*, a metal) into a siloxane chain influences many of its physico-chemical properties. For example, the thermal stability

of $-\text{Si}-\text{O}-\text{Si}-$ polymers can be modified by changing the electronic nature of the

bonding. The more ionic the bonding (or in the case of a covalent bond, the more polarized) the higher is the thermal stability. Thus substitution of a proportion of the

$\begin{array}{c} | \\ -\text{Si}-\text{O}- \\ | \end{array}$ units with $\begin{array}{c} | \\ -\text{M}-\text{O}- \\ | \end{array}$ ones (where M is a metal atom more electropositive than silicon) leads to an increase in $\begin{array}{c} | \\ -\text{Si}-\text{O}- \\ | \end{array}$ bond polarity, which is reflected in a rise in

the polymer degradation temperature. In addition, intermolecular forces, which are particularly weak in organopolysiloxanes, are enhanced as a result of the introduction of a metal (an agent capable of interacting coordinatively) which again has a substantial influence on polymer stability since it reduces (due to the formation of cyclic systems) its susceptibility to degradation^{4,5}.

Studies on polymetalloorganosiloxanes were initiated by Andrianov, who (together with his co-workers) concentrated upon the synthesis of these polymers and the determination of their physico-chemical properties^{3,6,7}. The practical application of these compounds has, however, not been reported. This stimulated us to attempt to use polymetalloorganosiloxanes as stationary phases in gas-solid chromatography (GSC). Of interest in this context is the fact that metal atoms present in siloxane chains are capable of interacting coordinatively with unsaturated compounds or those containing heteroatoms having lone electron pairs (this is clearly reflected in the separation ability of chromatographic packings^{8,9}). The π -complexes formed during the chromatographic process enable unsaturated compounds to be separated from alkane analogues. The prerequisites are full reversibility of the complex formation reaction and a high rate of the reaction, in order to establish equilibrium at a minimal value of the height equivalent to a theoretical plate (HETP), which has a significant effect on column efficiency.

EXPERIMENTAL

Synthesis of polymetallophenylsiloxanes

Several syntheses of polymetalloorganosiloxanes have been reported, for metals such as Al, Ti, Sn, Ge, Pb, Bi, Sb, V, Ni, Cu, Zr, Mg, Co, Fe and Cr^{3,6,7,10,11}. On the basis of these results, syntheses were performed of polymers containing Mg¹², Cu³ and Cr¹³ as well as of La and Nd which had not previously been described. Pure polyphenylsiloxane was also prepared for comparison purposes. The synthesis of these compounds is multistage and consists in the exchange reaction between the sodium salt of phenylsiloxane and a salt of a polyvalent metal. The first stage is the hydrolysis of the starting silane (phenyltrichlorosilane in this case). Then, the monosodium salt, which is the starting material for further syntheses¹⁴, is obtained from the reaction with a stoichiometric amount of sodium hydroxide.

Polylanthanophenylsiloxane was prepared as follows. Ten grams of polyphenylsiloxane sodium salt were dissolved in dry benzene (50 cm³) and placed in a three-necked flask equipped with a stirrer, a dropper and a reflux condenser. Then, 8.9 g La(NO₃)₃ dissolved in 50 cm³ of absolute alcohol were added during 2 h with constant stirring. After complete of the addition, the system was heated under reflux for 16 h. Then, solvents were removed by using a vacuum evaporator. The bright yellow vitreous mass obtained was extracted with dry benzene in a Soxhlet apparatus for 16 h. The yield of polymer (after benzene evaporation) was 7.6 g.

TABLE I
ELEMENTAL ANALYSIS OF POLYMERS

Polymer	Element (wt. %)				Molar ratio	
	C	H	Si	M	Si/M	C/Si
PCrPhS	48.45	3.51	18.94	3.11	9.48	5.98
PCuPhS	43.55	3.81	16.68	7.31	5.16	6.10
PMgPhS	44.18	4.33	19.05	6.45	2.58	5.49
PLaPhS	47.68	3.71	17.97	8.12	10.92	6.03
PNdPhS	46.37	3.82	18.04	9.31	9.92	6.03
PPhS	50.35	3.08	20.07	—	—	5.90

The following polymetallophenylsiloxanes were prepared similarly: polycopperphenylsiloxane (PCuPhS), polychromophenylsiloxane (PCrPhS), polylanthanophenylsiloxane (PLaPhS), polyneodymophenylsiloxane (PNdPhS), polymagnesiumphenylsiloxane (PMgPhS) and polyphenylsiloxane (PPhS). The polymers were characterized by elemental analysis for C, H, Si and M (*i.e.*, metal) (Table I), molecular weight determination and thermogravimetry. Since preliminary experiments had shown that polyneodymosiloxane behaved, from a chromatographic point of view, identically to polylanthanosiloxane, a full chromatographic characterization was performed only for the latter polymer.

Silicon and metals were determined according to the procedure of Andrianov *et al.*¹⁵, which consists in dissolving the polymer in H₂SO₄ containing KIO₃, followed by SiO₂ precipitation and determination of its mass. The filtrate was concentrated and then the metal concentration was determined by titration with EDTA in the presence of an indicator.

The quite high solubility of all the polymers in benzene has enabled determination of their molecular weights by osmometry (Table II). The constants of the ap-

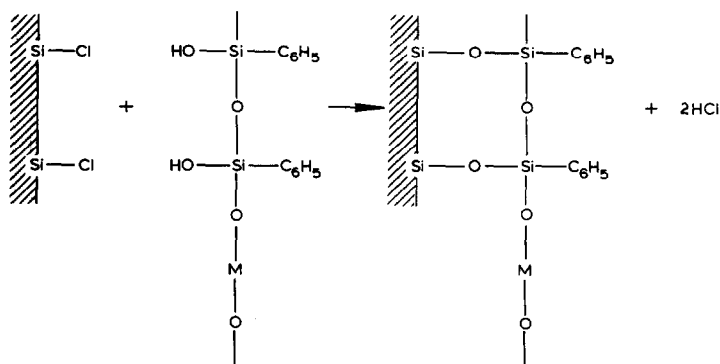
TABLE II
MOLECULAR WEIGHTS AND DEGRADATION TEMPERATURES

	PCrPhS	PCuPhS	PMgPhS	PLaPhS	PNdPhS	PPhS
Molecular weight	3064	4280	1806	7032	5661	3721
Degradation temperature (°C)	220	419	220	505	419	220

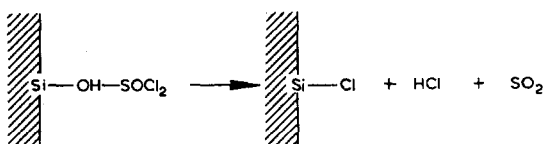
paratus used were determined by using bibenzoyl, C₆H₅COCOC₆H₅. In the same table are given the decomposition temperatures of the polymers as determined by thermogravimetric analysis. It is seen that the temperatures depend on both the molecular weight and the composition of the polymers.

Column packings

The described polymers were used in the form of chemically bonded phases. The bonding reaction occurred between hydroxyl groups in the siloxane chain and the chlorinated surface of silica:



Thionyl chloride, SOCl_2 , was employed as a chlorinating agent¹⁶:



Silica was dried at 180°C for 6 h prior to the reaction. The chlorination was carried out under moisture-free conditions by using 30% SOCl_2 solution in dry benzene and a reaction time of 12 h. Then the benzene solution of SOCl_2 was decanted and the solid was washed with benzene ($4 \times 75 \text{ cm}^3$). The resulting material was contacted with 50 cm^3 of a 20% benzene solution of a polymer and refluxed for 16 h. After washing, each packing was extracted with benzene (6 h) and dried under vacuum. It is expected that not all hydroxyl groups of a polymer will react with chlorine bonded to the silica surface. Therefore, the remaining OH groups were deactivated with dry methanol, followed by treatment with trimethylchlorosilane. The packings were then dried at 150°C for 6 h and the resulting materials were used for surface area determination. Finally, the packings were conditioned in a column at 180°C for 12 h. Results of analyses are shown in Table III.

TABLE III

CHARACTERIZATION OF COLUMNS

The surface area of the starting silica was $360 \text{ m}^2/\text{g}$.

No.	Packing	Elemental analysis (%)		Chemically bonded phase (% w/w)	Surface area, (m^2/g)
		C	H		
1	PCrPhS	2.30	0.13	4.74	288
2	PCuPhS	1.03	0.07	2.36	308
3	PLaPhS	2.14	0.10	4.48	301
4	PMgPhS	1.85	0.06	4.25	293
5	PPhS	1.90	0.07	3.77	290

Apparatus

Experiments were carried out on a Chromatron gas chromatograph Model GCHF 18.3 equipped with a flame ionization detector. The columns (100 × 0.4 cm) were made of stainless steel. The thermostat was provided with an additional thermometer (accurate to ±0.1°C) and a mercury manometer enabling measurement of pressure at the column inlet with an accuracy of 1 mmHg was included in the carrier gas (argon) system. Retention times were measured by means of a 20-MHz timer counter, Model C-549A (Meratronik, Poland) with an accuracy of 0.01 sec. Samples were injected with a 2- μ l Hamilton syringe.

Surface areas were measured on a Gravimat sorptometer (Sartorius, G.F.R.) using nitrogen as adsorbate at -195°C. Elemental analyses were carried out on a Perkin-Elmer Model 240 Elemental Analyzer. Molecular weights were determined on a Dampf-Druck osmometer (Knauer, G.F.R.). Thermogravimetric analysis was performed on a Q-Derivatograph (MOM, Hungary).

Reagents

Phenyltrichlorosilane (PhTCS) and trimethylchlorosilane (TMCS) were purchased from Ventron (U.S.A.) and the silica gel 60 (0.2–0.25 mm) support from Macherey, Nagel & Co., G.F.R.. All other reagents were manufactured by POCh Gliwice (Poland).

RESULTS AND DISCUSSION

The polymetallophenylsiloxanes studied are distinguished by high resistance to hydrolysis and high thermal stability. Their solubility in many organic solvents such as benzene, chloroform and carbon tetrachloride enables ready impregnation of supports. The presence of hydroxyl groups at the silicon atoms makes possible chemical bonding between the polymer and silica surfaces. This suggests applications of these compounds also in high-performance liquid chromatography (HPLC).

The surface area of silica markedly decreases after bonding to the polymer. The decrease is of the same magnitude in all cases and ranges from 70 m²/g for PCrPhS to ≈ 50 m²/g for PCuPhS. The reduction is caused by a modification of the silica surface with bonded polymer, and by blocking a proportion of the micropores with the "large" polymer molecules. Since only a part of the surface (determined by sorption of "small" nitrogen molecules) is accessible to the polymer molecules and the fraction of the surface penetrated by the "large" polymer molecules is unknown, it is impossible to calculate the surface coverage on the basis of elemental analysis data (% C).

We have measured HETP values, using hexane and benzene as adsorbates, and we have found that minimum values of HETP occur at carrier gas flow-rates between 4.5 and 5.5 cm/sec, *i.e.*, 23–27 cm³/min, and are in the range 1.05–1.46 mm, *i.e.*, 950–650 theoretical plates.

In order to test the separation ability of these packings we have carried out measurements of the retention for eighteen hydrocarbons. Relative retention volumes, *r*, calculated from specific retention volumes, ^{PT}V_A (cm³/m²)*, are listed in Table

* ^{PT}V_A = [(t_R - t_M)F₀j/w_sA_s] (p₀/760) (T_c/T_M), where t_R = gross retention time, t_M = dead time, F₀ = gas flow-rate from column, j = column pressure gradient correction factor, w_s = weight of adsorbent in column, A_s = specific surface area of adsorbent, p₀ = column outlet pressure, T_c = absolute column temperature and T_M = flow meter temperature.

TABLE IV
RELATIVE RETENTION VOLUMES, r , AT 120°C

Hydrocarbon	Packing				
	PCuPhS	PCrPhS	PPhS	PMgPhS	PLaPhS
Pentane	1.00	1.00	1.00	1.00	1.00
1-Pentene	1.24	1.19	1.14	1.14	1.16
Hexane	1.00	1.00	1.00	1.00	1.00
1-Hexene	1.27	1.25	1.20	1.18	1.18
<i>cis</i> -2-Hexene	1.48	1.46	1.40	1.40	1.38
<i>trans</i> -2-Hexene	1.38	1.36	1.29	1.29	1.30
<i>cis</i> -3-Hexene	1.44	1.40	1.36	1.36	1.34
<i>trans</i> -3-Hexene	1.39	1.36	1.29	1.30	1.29
1-Hexyne	3.01	2.70	2.58	2.58	2.45
2,4-Hexadiene	2.89	2.72	2.51	2.52	2.50
1,5-Hexadiene	1.54	1.50	1.23	1.23	1.21
Heptane	1.00	1.00	1.00	1.00	1.00
1-Heptene	1.27	1.25	1.20	1.20	1.19
Cyclohexane	1.00	1.00	1.00	1.00	1.00
Cyclohexene	1.62	1.55	1.42	1.42	1.40
1,3-Cyclohexadiene	1.89	1.76	1.68	1.69	1.68
1,4-Cyclohexadiene	2.28	2.15	2.06	2.06	2.07
Benzene	2.13	2.05	1.91	1.88	1.90

TABLE V
RETENTION INDICES, I , CAPACITY RATIOS, k' , AND $-\delta\Delta G_{\text{spec}}$ VALUES FOR PACKINGS CONTAINING PCuPhS AND PMgPhS AT 140°C

Hydrocarbon	I_{Cu}	I_{Mg}	k'_{Cu}	k'_{Mg}	$k'_{\text{Cu}}/k'_{\text{Mg}}$	$-\delta\Delta G_{\text{spec}}$
						(kcal/mol)
Pentane	500	500	1.38	1.19	1.15	0.122
1-Pentene	518	514	1.51	1.28	1.17	0.178
Hexane	600	600	2.32	1.96	1.18	0.152
1-Hexene	632	621	2.74	2.19	1.25	0.226
<i>cis</i> -2-Hexene	654	644	3.07	2.45	1.25	0.230
<i>trans</i> -2-Hexene	639	629	2.84	2.28	1.24	0.228
<i>cis</i> -3-Hexene	645	635	2.94	2.34	1.25	0.238
<i>trans</i> -3-Hexene	639	628	2.85	2.27	1.25	0.237
2,4-Hexadiene	743	722	4.89	3.62	1.35	0.342
1,5-Hexadiene	657	637	3.13	2.37	1.32	0.317
1-Hexyne	760	718	5.34	3.55	1.50	0.397
Heptane	700	700	3.90	3.24	1.20	0.187
1-Heptene	742	728	4.60	3.54	1.19	0.260
Cyclohexane	639	637	2.84	2.37	1.19	0.163
Cyclohexene	698	685	3.86	3.01	1.28	0.246
1,3-Cyclohexadiene	730	713	4.55	3.45	1.31	0.286
1,4-Cyclohexadiene	758	735	5.28	3.87	1.36	0.306
Benzene	747	730	4.97	3.78	1.31	0.293

IV. Analysis of the results indicates that unsaturated compounds (those with π -electrons) exhibit longer retention times on the chromium-(PCrPhS) and copper-containing (PCuPhS) packings. A comparison of relative retention volumes enables the packings to be placed in the following order of decreasing affinity for olefins: PCuPhS > PCrPhS > PPhS \geq PMgPhS \geq PLaPhS. The sequence is maintained over the whole temperature range studied, *i.e.*, from 120 to 160°C.

The central position of polyphenylsiloxane (PPhS) in the above series, enables a clear division of the packings into two groups. The first includes copper- and chromium-containing packings which show an affinity for unsaturated compounds, where π -electron interactions are essential to the chromatographic process, *e.g.*, PCuPhS and such compounds as 1-hexyne, hexadienes and cyclohexadienes. The second group of packings (PPhS, PMgPhS and PLaPhS) does not show π -electron type interactions because of the absence of a complex-forming agent or the presence of a metal with very poor complex-forming properties (PLaPhS). This classification is confirmed by the retention indices for PCuPhS and PMgPhS and values of the capacity ratios, k' , listed in Table V. The ratio of $k'_{\text{Cu}}/k'_{\text{Mg}}$ (ranging from 1.15 to 1.50) is a measure of the differences discussed.

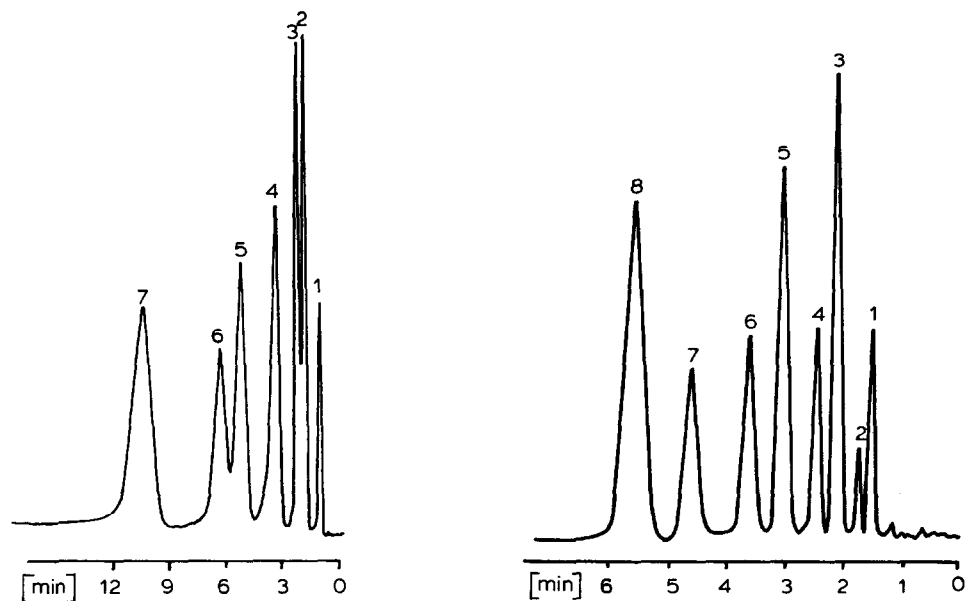


Fig. 1. Analysis of chloroethane derivatives on PMgPhS packing. T_k (column temperature, °C) = 140.4°C; F_0 (gas flow-rate from column, ml/min) = 31.0 ml/min. Peaks: 1 = chloroethane; 2 = 1,1-dichloroethane; 3 = 1,1,1-trichloroethane; 4 = 1,2-dichloroethane; 5 = 1,1,2-trichloroethane; 6 = 1,1,1,2-tetrachloroethane; 7 = 1,1,2,2-tetrachloroethane.

Fig. 2. Separation of a mixture of alkanes and alkenes on PCrPhS packing. T_k = 158.6°C; F_0 = 15.6 ml/min. Peaks: 1 = heptane; 2 = 1-heptene; 3 = octane; 4 = 1-octene; 5 = nonane; 6 = 1-nonene; 7 = decane; 8 = 1-decene.

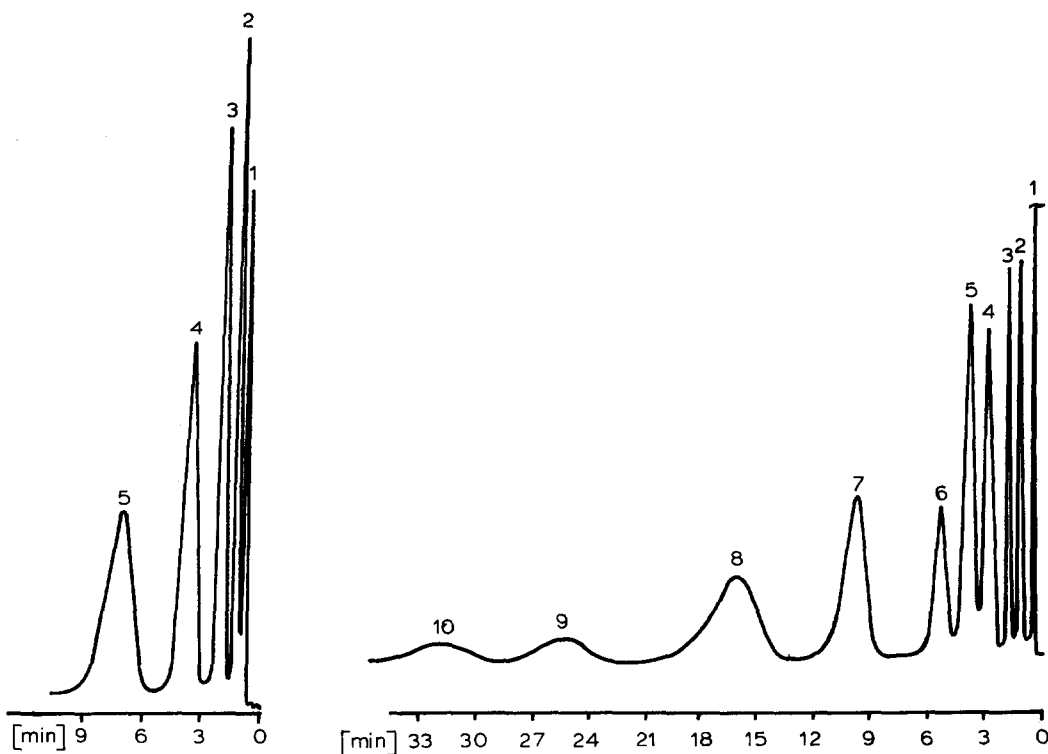


Fig. 3. Separation of ketones on PCrPhS packing. $T_k = 130.8^\circ\text{C}$; $F_0 = 26.1$ ml/min. Peaks: 1 = 2-butanone; 2 = 2-pentanone; 3 = 2-hexanone; 4 = heptanone; 5 = 2-octanone.

Fig. 4. Analysis of polycyclic aromatic hydrocarbons (PAHs) on PCuPhs packing. $T_k = 230^\circ\text{C}$; $F_0 = 31.0$ ml/min. Peaks: 1 = solvent (chloroform); 2 = indene; 3 = naphthalene; 4 = diphenyl; 5 = acenaphthene; 6 = fluorene; 7 = anthracene; 8 = *ortho*-terphenyl; 9 = pyrene; 10 = *para*-terphenyl.

The reason for the choice of polymagnesiumphenylsiloxane as a reference phase for polycopperphenylsiloxane is the similarity in ionic radii of Cu and Mg. Thus, with the same charge, the electrostatic interactions (of dipole-induced dipole type) will be identical¹⁷.

The change in free energy value, $\delta\Delta G$, on going from a transition metal (Cu)-containing polymer to a main group metal (Mg)-containing polymer can be used as a measure of the coordinative interaction between copper and olefins:

$$\delta\Delta G_{\text{spec.}} = \Delta G_{\text{Cu}} - \Delta G_{\text{Mg}} = -RT \ln \frac{p^T V_{A(\text{Cu})}}{p^T V_{A(\text{Mg})}}$$

The values given in Table V point to the occurrence of specific interactions between copper and alkenes during the chromatographic process. From an analysis of the retention data the following conclusions can be drawn:

(1) The strongest interactions of olefins were observed toward copper- and chromium-containing polymers;

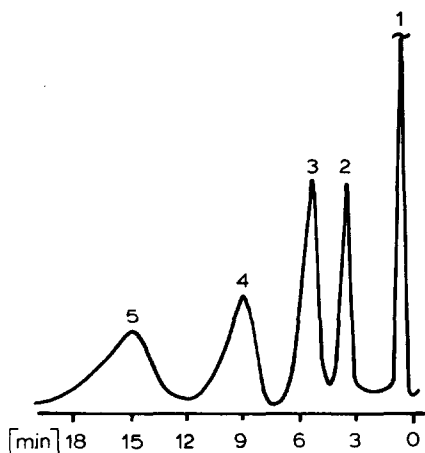


Fig. 5. Separation of high boiling alkanes on PCuPhS packing. $T_k = 270^\circ\text{C}$; $F_o = 19.6$ ml/min. Peaks: 1 = chloroform; 2 = octadecane; 3 = eicosane; 4 = docosane; 5 = tetracosane.

(2) The strength of the interaction depends on the degree of unsaturation of the olefin;

(3) *cis*-Isomers interact more strongly than *trans*-isomers;

(4) In all cases the interactions are much weaker than those described in the literature for systems containing metals of Group 8 of the Periodic Table.

The data presented in Tables IV and V indicate the potential of these poly-metallophenylsiloxane packings as stationary phases for chromatographic analysis. Examples of separations are shown in Fig. 1 for chloro derivatives of alkanes, in Fig. 2 for alkane and alkene mixtures and in Fig. 3 for ketones. An advantage of the polymers, particularly PCuPhS, PCrPhS and PLaPhS, is their high thermal stability. This extends the range of possible applications to analysis of high boiling compounds (up to $\approx 400^\circ\text{C}$). Examples of such applications are given in Fig. 4 (polyaromatic hydrocarbons) and in Fig. 5 (high boiling alkanes). Prior to the analyses, the columns had been conditioned at 340°C for 12 h. The chromatograms indicate the good separation, with sharp and symmetric peaks, as well as the relatively short analysis time.

REFERENCES

- 1 J. K. Haken, *J. Chromatogr.*, 73 (1972) 419.
- 2 J. K. Haken, *J. Chromatogr.*, 141 (1977) 247.
- 3 A. A. Zhdanov, K. A. Andrianov and M. M. Levitskii, *Vysokomol. Soedin., Ser. A*, 18 (1976) 2264.
- 4 M. F. Lappert and G. J. Leigh, *Developments in Inorganic Polymer Chemistry*, Elsevier, Amsterdam, 1962.
- 5 F. G. A. Stone and W. A. G. Graham, *Inorganic Polymers*, Academic Press, New York, 1962.
- 6 K. A. Andrianov, *Polimery s neorganicheskimi glavnyimi tsepyami molekul*, Izd. AN SSSR, Moskva, 1962.
- 7 A. A. Zhdanov, K. A. Andrianov and M. M. Levitski, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1974) 653.
- 8 W. Szczepaniak, J. Nawrocki and W. Wasiak, *Chromatographia*, 12 (1979) 484.
- 9 W. Szczepaniak, J. Nawrocki and W. Wasiak, *Chromatographia*, 12 (1979) 559.

- 10 M. Bartholin and A. Guyot, *C.R. Acad. Sci. Ser. C*, 264 (1967) 1694.
- 11 M. Bartholin and A. Guyot, *J. Chim. Phys. Phys.-Chim. Biol.*, 67 (1970) 835.
- 12 A. A. Zhdanov, K. A. Andrianov, I. M. Kolesnikov, G. M. Panchenkov, M. M. Levitskii and N. N. Belov, *Vysokomol. Soedin., Ser. B*, 17 (1975) 149.
- 13 T. P. Avilova, V. T. Bykov and L. A. Kondratenko, *Vysokomol. Soedin., Ser. A*, 8 (1966) 14.
- 14 K. A. Andrianov and A. A. Zhdanov, *Dokl. Akad. Nauk SSSR*, 114 (1957) 1005.
- 15 K. A. Andrianov, T. N. Ganina and Ye. N. Khrustaleva, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk*, (1956) 798.
- 16 D. C. Locke, J. T. Schermund and B. Benner, *Anal. Chem.*, 44 (1972) 90.
- 17 J. Nawrocki, *Ph.D. Thesis*, A. Mickiewicz University, Poznań, 1977.