

CHROMSYMP. 398

CYANOSILICONES AS STATIONARY PHASES IN GAS CHROMATOGRAPHY

III. SYNTHESIS, CHARACTERIZATION AND EVALUATION

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SUMMARY

Methods for the reproducible synthesis of curable cyanosilicone stationary phases have been developed. Different paths of synthesis has been compared, and the influence of these on the phase properties examined. A series of phases having 33, 50, 60, 75% cyano substitution, respectively, was prepared, in a manner so as to avoid the formation of amides. The effects of the use of methyltolyl, bis(tolyl) and methylvinyl blocks and bis(dimethyl)silylarylene units on cross-linking of cyano-containing organosiloxanes were examined. These phases were characterized by various chromatographic, spectroscopic and thermal analytical methods. Columns coated with the phases were tested with respect to efficiency, activity and thermal stability. The usefulness of the phases for selective separations of fatty acid methyl esters is demonstrated both with standards and actual samples of different origins.

INTRODUCTION

Polar silicone stationary phases are often required in capillary gas chromatography (GC) for the separation of positional and/or stereoisomers. The potential selectivity of a column coated with such a phase can be utilized when the column shows a combination of efficiency, thermostability and inertness towards adsorptive substances. The stationary phase should be homogeneous and its structure reproducible. Earlier polar stationary phases and columns exhibited relatively poor chromatographic properties. Better results were often achieved with an efficient non-polar column than with a selective column of relatively low efficiency¹. Recently, however, the quality of polar columns has been much improved.

The physical stability of a film of stationary phase in a column is greatly dependent on its viscosity. Physical rearrangements on the surface, resulting in column deterioration, are thus more likely for a film of silicones of low viscosity than for corresponding highly viscous gums. Methylsilicone gums are particularly advantageous in this context, since a high viscosity is maintained also at elevated temperatures, e.g., 300°C. With increasing thickness, films of methylsilicone gums become

less stable. For cyanosilicones, the viscosity decreases dramatically with increasing temperature², and thus in this case the use of gums will not substantially improve thermal stability. With the advent of stationary phase immobilization, the use of cyanosilicone stationary phases at elevated temperatures has become feasible³⁻⁸. A further improvement in the performance of such columns is achieved when the capillaries, prior to coating, are treated at high temperatures with cyanopropyl-substituted cyclic siloxanes⁹. This provides a surface that is wettable by the stationary phase and which at the same time becomes efficiently deactivated. It should be mentioned that different batches of fused-silica capillary tubing may have different properties. Among other things, the surface adsorption activity can vary, and the need for deactivation thus varies between batches.

In previous parts of this series^{4,5}, the synthesis and properties of some new types of curable cyanosilicone stationary phases were described. The influence of some different approaches to the synthesis of low-molecular-weight intermediates on the properties of the stationary phase has now been studied. The resulting gum phases were characterized by a number of different spectroscopic and chromatographic methods.

Our intention was to meet the increasing demands from users regarding reproducibility of the chromatographic results by providing well characterized polar stationary phases in high-quality capillary columns. It may be pointed out, however, that reproducibility of analysis is not solely a question of column properties, but also of instrumentation that allows high precision.

EXPERIMENTAL

Organosilicone synthesis

Reagents

Bis(cyanopropyl)dichlorosilane (Lot 33549), methyltolylidichlorosilane (b.p. 161°C/7 mmHg), 1,1,3,3-tetramethyl-1,3-divinyl-disilazane (Lot 32979), 1,4-bis(hydroxydimethylsilyl)benzene (Lot 33194) and methylvinylidichlorosilane were obtained from Petrarch Systems Inc. (Bristol, PA, U.S.A.), dimethyldichlorosilane and bis(α,α -dimethylbenzyl) peroxide (DCP) from Merck (Darmstadt, F.R.G.), bis(tolyl)dimethoxysilane and azo-*tert.*-butane (ATB) from Dr. M. L. Lee, Utah, and tetramethylammonium hydroxide pentahydrate (97%) and zinc oxide from Janssen Chimica (Beerse, Belgium). Solvents of analytical grade were used.

Preparation of intermediates

(a) *Basic reversed hydrolysis of dichlorosilanes*¹⁰. To a mixture of dichlorosilanes (0.04 mol) and methylene chloride (50 ml), cooled in an ice-salt bath (-3°C), a 6 M solution of ammonia (25 ml) was added dropwise (2 h) with vigorous stirring under an atmosphere of nitrogen. After separation from the aqueous layer, the methylene chloride layer was washed several times with distilled water.

(b) *Reversed hydrolysis of dimethoxysilanes*. The chlorosilanes were converted into the corresponding methoxysilanes by treatment with an excess of methyl orthoformate^{11,12} with stirring at room temperature (70 h) and without aluminium chloride as catalyst. The mixture was distilled and redistilled under reduced pressure, the purity of the dimethoxysilane being finally examined by GC. To a mixture of dimethoxysilanes (0.04 mol) and acetonitrile (20 ml) in a reaction flask, equipped with

a condenser, was added distilled water (20 ml). The mixture was stirred under an atmosphere of nitrogen for 40 h to ensure complete hydrolysis of the silanes. After extraction with methylene chloride, the solvent was removed under vacuum.

(c) *Non-hydrolytic cyclization for the copolymerization of short blocks*¹³. Cyclization was performed separately for each dichlorosilane. Powdered and dried analytical-grade zinc oxide (0.05 mol) was suspended in acetonitrile (100 ml) in a reaction flask, equipped with a dropping funnel and a condenser. A mixture of the dichlorosilane (0.04 mol) in acetonitrile (50 ml) was added dropwise (1 h) with vigorous magnetic stirring and under an atmosphere of nitrogen at 0°C. After 2 h, the ice-bath was replaced by an oil-bath and the reaction mixture was refluxed for 20 min, cooled slowly and then allowed to stand for 15 h with stirring under an atmosphere of nitrogen. The cyclics were extracted with toluene and washed several times with distilled water.

(d) *Non-hydrolytic cyclization for copolymerization*¹⁴. All the reactants were already mixed in the cyclization step. The same procedure as in (c) was then followed.

(e) *Non-hydrolytic cyclization for copolymerization with a short-block "pure" cyclic*. The cyclization procedure in (c) was followed for the preparation of cyclics with mixed substituents. Methylvinylcyclopentasiloxane, later used to create short blocks in the polymer, was prepared by an acidic hydrolysis followed by distillation under reduced pressure.

*Polymerization*¹⁵⁻¹⁸

The high-boiling polymers were mixed in the desired ratio and placed in a flask fitted with a nitrogen inlet and a mechanical stirrer, which caused the prepolymer to be spread over the walls of the flask. Traces of water were evaporated by azeotrope formation with acetonitrile and, after allowing the mixture to cool to 80°C, it was examined by IR spectroscopy. If low boiling prepolymers, *i.e.*, methylvinylcyclopentasiloxane, were to be used, a distilled fraction was added at this point. After addition of the catalyst, tetramethylammonium hydroxide (TMAH) (0.01 wt. %), in the form of a 10% (w/v) solution in methanol, the polymerization mixture was allowed to equilibrate (3-4 h) at 85-95°C. The mixture was then rapidly heated to 150°C and maintained at this temperature for 10 min in order to destroy the catalyst.

End-capping

End-capping was effected by adding pure 1,1,3,3-tetramethyl-1,3-divinyl-disilazane to the polymer and stirring the mixture at 150°C for 3 h under an atmosphere of nitrogen^{19,20}.

Fractionation

End-capped polymers were dissolved in methylene chloride and precipitated by the addition of methanol to remove residual low-molecular-weight material and unreacted disilazane. Size exclusion chromatography was used to fractionate the polymers. A Styragel (100 Å) column (Waters Assoc., Milford, MA, U.S.A.), capable of separation up to MW 1000, was overloaded and the fraction in the exclusion volume was collected. The polymers were finally heated at 150°C under an atmosphere of nitrogen and stored in Pyrex vials.

Preparation of bis(γ -cyanopropyl)methylsilylenosiloxane copolymer

A non-hydrolytic process²¹, where alkoxy silanes were allowed to react with organosilanols, was utilized in the synthesis of a polymer, containing 33% bis(γ -cyanopropyl) groups on a polysilylenosiloxane backbone. Equal amounts of

bis(γ -cyanopropyl)dimethoxysilane (0.025 mol) and 1,4-bis(hydroxydimethylsilyl)benzene (0.025 mol) were stirred in a total absence of water under an atmosphere of nitrogen, at 0°C for 4 h. 10^{-2} wt. % TMAH was added, methanol was distilled off and equilibration, end-capping and fractionation of the polymer were carried out according to the procedure described.

Analysis of stationary phases

Thermal analysis. Thermogravimetry (TG) was carried out with a Perkin-Elmer TGS-2 instrument. Samples (10 mg) were heated at 10 or 20°C min⁻¹ from 30 to 300 or 700°C in a stream of nitrogen (5 ml min⁻¹).

Differential scanning calorimetry (DSC) was carried out with a Perkin-Elmer DSC-2c instrument. Samples (20 mg) were heated at 10°C min⁻¹ from 30 to 300°C in a stream of nitrogen (5 ml min⁻¹).

Pyrolysis gas chromatography-mass spectrometry (GC-MS) was performed on-line on apparatus constructed in this laboratory²². Thus, pyrolysed products (275°C) were trapped on silanized glass beads (liquid nitrogen), and transferred by heating on to a gas chromatograph (SE-52 column) that was programmed at 10°C min⁻¹ from 30°C. A Jeol JMS-D300 mass spectrometer was used as detector.

Characterization of polymers. IR spectra were recorded on a Perkin-Elmer 297 instrument. A sufficient amount of polymer was dispersed between two sodium chloride pellets to yield a light transmission of 10–80%. Each synthesis step was followed by IR spectroscopic analysis, to trace possible oxidation occurring in the phase.

Gel permeation chromatography (GPC) was carried out on two columns in series, filled with porous silica microspheres (PSM 60, PSM 1000), and with refractive index (RI) and UV detection. Molecular weight calibration was performed with a polystyrene standard.

¹H NMR spectra were measured on solutions of samples in deuteriochloroform and recorded on a Jeol FX100 NMR spectrometer.

Column preparation

Fused-silica tubes with I.D. of 0.05 mm (SGE, Victoria, Australia), 0.22 mm (Quartz et Silice, Paris, France), 0.25 mm (Hewlett-Packard, Avondale, PA, U.S.A.) or 0.22 mm (SpecTran, Sturbridge, MA, U.S.A.) were used. The pretreatment was as previously reported^{4,5} except that a 2–5% solution (instead of 20%) of cyclic cyanosiloxane was used in the dynamic coating prior to chemical surface modification. Coating was thus carried out with 50CN-cyclic (cyanopropyl-methylcyclorosiloxane) in toluene or 100CN-cyclic (bis-cyanopropylcyclorosiloxane) in methylene chloride. The cyanosilicone gum phases synthesized in this laboratory (Table I) were dissolved in methylene chloride for the static coating.

Coating of 0.05 mm I.D. columns

A number of columns (4.5 m × 0.05 mm I.D.) were prepared according to the same pretreatment and coating procedure as used for ordinary capillary columns. These columns could be used in conventional gas chromatographs. The PTFE tubing used for connections in the column preparation was of a thinner type than usual, *i.e.*, 0.30 mm I.D., 0.60 mm O.D. Furthermore, a piece of PTFE at the closed end of the column made it easier to determine when the evaporation was completed. Silicone wafers²³ were used to ensure smooth edges when cutting the fused-silica capillary tubing.

Cross-linking methods

(a) Prior to use, the peroxide DCP was recrystallized from ethanol-water (72:28), and then dissolved in methylene chloride. A portion of this solution was added to the coating solution to give a peroxide concentration of 2–5%, based on the amount of stationary phase to be coated. After coating, the phase was cured by a dynamic procedure, as described earlier^{4,5}.

(b) The azo compound ATB was added to the polymer after coating the column, which was thus flushed with nitrogen, saturated with ATB vapour, for 1 h, curing being carried out at 220°C for 1 h²⁴.

(c) Radiation from a high-voltage electron source (10–25 Mrad) was used to cross-link gum phases having up to 50% cyano groups.

(d) Ozone from an ozone generator was used to cross-link gum phases at 150°C for 15 min, after the column had been filled with an ozone-oxygen mixture and sealed^{25,26}.

(e) A room-temperature cross-linking procedure³ was performed on a silanol-terminated gum phase. After coating, the column was thus filled with nitrogen, saturated with tetrachlorosilane, sealed and allowed to stand for 5 h at room temperature. The remaining tetrachlorosilane was then removed by passage of dry nitrogen for 5 h. Dry ammonia gas was allowed to fill the column, which was then sealed and left at room temperature for 12 h. Thorough nitrogen flushing, followed by rinsing with pentane, was performed before the column was conditioned. Finally, the column was slowly rinsed (10 h) with 10 ml methylene chloride, followed by flushing with nitrogen for at least 5 h.

Column evaluation was accomplished with Carlo Erba 4160 or Hewlett-Packard 5790 gas chromatograph, equipped with flame-ionization detectors. Hydrogen was used as carrier gas at a linear velocity of 50 cm sec⁻¹ (90°C). The results were computed on a Hewlett-Packard integrator 3390 A. The amount of the different compounds analyzed was *ca.* 1 ng per peak on the chromatograms. Splitless injections were used, and for the samples dissolved in methylene chloride, a plug of *n*-hexane was injected together with the sample.

RESULTS AND DISCUSSION

The cyano group may be considered as one of the most stable polar substituents available today on a siloxane backbone. Commercial cyano silicone phases, however, exhibit certain drawbacks, such as a lack of reproducibility between batches, low viscosity and differences in consistency and polarity; they may be contaminated or partly oxidized. The reason for the popularity of these phases can be found in the demand for selective interactions, such as charge transfer, in the separation of different isomers.

Reproducibility of the product involves homogeneous mixing of different substituents along the siloxane chain, chemical stability during the synthesis and storage of the gum, as well as chemical and physical stability in the column. Efficient columns can be prepared from highly viscous phases or gums, and stability is achieved by cross-linking to give an elastic rubber. However, the choice of substituents to facilitate the cross-linking may strongly influence the thermal stability of the column. The characterization of cyano-containing polysiloxanes described in earlier papers^{4,5} en-

TABLE I
ORGANOSILOXANE GUMS CONTAINING CYANO GROUPS

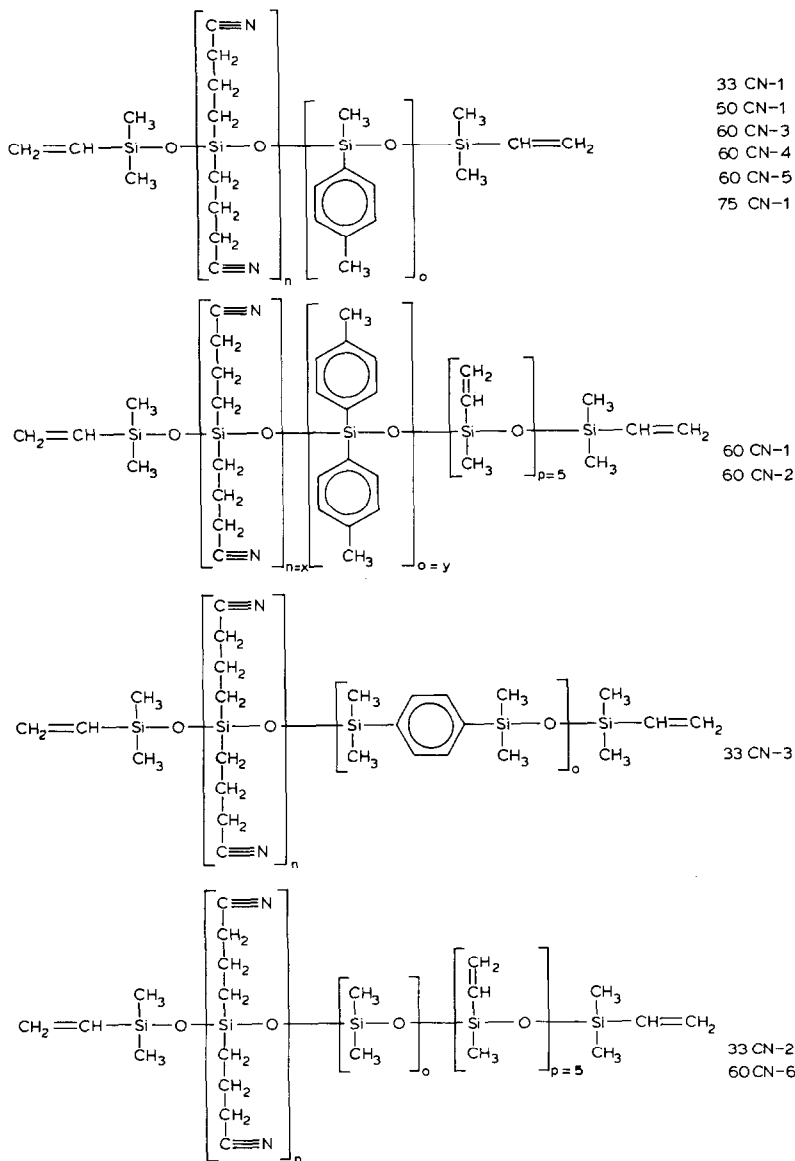
Polymer	Substituents on the siloxane chain (mol %)					Monomer used	Synthesis pathways	CN (mol %) by ¹ H NMR
	Cyanopropyl from bis(cyanopropyl)	Methyl from dimethyl	Tolyl from methyltolyl	Tolyl from bis(tolyl)	Vinyl from methylvinyl			
33CN-1	33		67			Chloro	Basic reversed hydrolysis	
33CN-2	33	64			3	Chloro	Non-hydrolytic cyclization, mixed substitution in cyclics + vinyl cyclic as a block	46
33CN-3	33	67*				Methoxy silanol	Non-hydrolytic condensation of alkoxy and silanol groups	43
50CN-1	50		50			Chloro	Basic reversed hydrolysis	50
60CN-1	60	33		5	2	Methoxy	Non-hydrolytic cyclization (different cyclics)	
60CN-2	60	33		5	2	Methoxy	Reversed hydrolysis	
60CN-3	60		40			Chloro	Basic reversed hydrolysis	
60CN-4	60		40			Chloro	Non-hydrolytic cyclization, mixed substitution in cyclics	
60CN-5	60		40			Chloro	Non-hydrolytic cyclization, mixed substitution in cyclics	57
60CN-6	60	37			3	Chloro	Non-hydrolytic cyclization, mixed substitution in cyclics + vinyl cyclics as blocks	60
75CN-1	75		25			Chloro	Basic reversed hydrolysis	74

* From 1,4-bis(hydroxydimethylsilyl)benzene.

couraged us to examine more closely the influence that the synthetic path has on the performance of the gum. A series of gums containing 60% cyanopropyl substitution was thus synthesized according to different synthetic paths (Table I). The structures of the phases prepared are shown in Scheme I.

Synthesis of organosiloxanes containing cyano groups

Dichloro- and dimethoxysilanes were used as monomers. In order to minimize



Scheme I. The structures of the phases prepared. 60CN-1 and 60CN-2 also contain dimethyl substitution.

the influence of variations in starting materials, bis(cyanopropyl)dichlorosilane from only one batch was used. With chlorosilanes there is a risk of deleterious effects, caused by the formation of HCl. Jones *et al.*⁸ reported that a complex between HCl and the cyano function can be formed which is difficult to remove. The presence of carboxamide groups in several commercial cyanosilicones has also been demonstrated⁸. All the syntheses in this study were closely followed by IR analysis in order to trace possible oxidation of the phase. Commercially available cyanopropylsilanes may contain *ca.* 1% of chloropropyl-substituted material, and it is difficult to purify the silane further²⁷. The synthesis of monomer was beyond the scope of this study, but it certainly should be considered when the improvement in stationary phase performance is undertaken.

Preparation and analysis of intermediates. Some different approaches are available in which HCl is not liberated during the synthesis. The method most frequently used is probably a straight hydrolysis from dimethoxysilanes^{11,12}. This method was used for the preparation of phase 60CN-2. It may be difficult to obtain a complete conversion of methoxy groups without adding a strong acid or base¹⁰. Small amounts of bis(tolyl)- and methylvinylsilanes were used to facilitate cross-linking of this phase. A non-hydrolytic procedure by the use of metal oxide is another possibility for the preparation of intermediates without the formation of HCl:

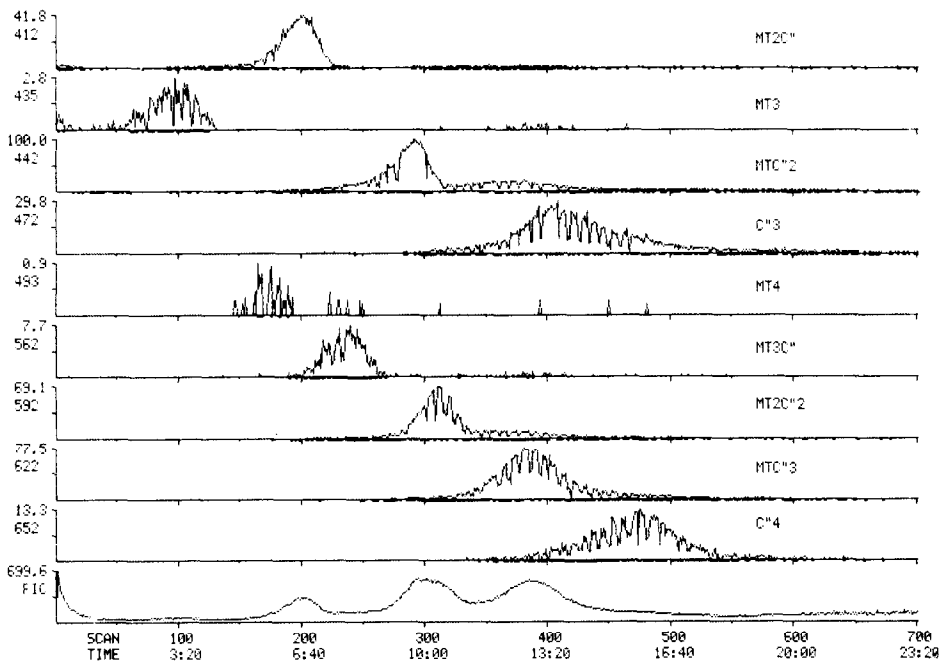
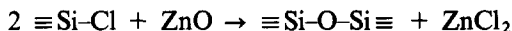


Fig. 1. Mass chromatogram of cyclic intermediates with mixed substituents, in the synthesis of 60CN-5 gum. Substituents: MT = methyltolyl; C'' = bis(γ -cyanopropyl). The masses correspond to a characteristic fragment from each cyclic, at 70 eV.

Takiguchi *et al.*¹³ reported that, when they were using a 10% excess of ZnO and an inert solvent for the reaction of diphenyldichlorosilane, the product obtained was almost pure hexaphenylcyclotrisiloxane.

Cyclics thus prepared can comprise only one type of substituents in each cyclic siloxane, forming a type of block polymer upon subsequent polymerization, *e.g.*, phase 60CN-1. A problem which can arise is the different reaction rates of the cyclosiloxanes involved, resulting in an inhomogeneous polymer. A more homogeneous polymer can be obtained from mixed substitution among the units in the cyclic siloxanes, forming "hybrid" cyclics, such as phases 60CN-4 and 60CN-5. It is possible that a multitude of cyclics are formed, if the mutual reactivity of the monomers differs¹⁴. When using this method, we found by MS analysis that the intermediates formed in phase 60CN-5 contained cyclotetrasiloxane and cyclotrisiloxane in about equal amounts, Fig. 1 [MT = methyltolyl, C'' = bis(γ -cyanopropyl)]. The highest concentrations were found for the C₂' MT, C₃' MT and C₂' MT₂ intermediates. Corresponding cyclics with only one type of substituents were found only in very low amounts.

Phase 60CN-3 was prepared according to earlier methods^{4,5}. By this basic reversed hydrolysis, HCl will be formed. When the reaction was performed in an atmosphere of pure nitrogen and below 0°C, no change in substituents could be detectable by IR analysis. The silicones produced in this manner had earlier proved to be stable and useful as stationary phases.

Quantitation of the mol % cyano substitution achieved in corresponding gums was obtained from ¹H NMR spectra and the results are presented in Table I. The percentages found should be compared to the selectivity characteristics found for columns coated with these phases.

Figs. 2 and 3 verify, by IR and ¹³C NMR spectroscopy respectively, that no carboxamide groups are detected in the phases synthesized here. The last spectrum presented in Fig. 2 shows that the phase composition was unaltered also after cross-linking with 5% DCP on a sodium chloride plate. Two gum phases, 60CN-3 and 60CN-4, were analyzed by GPC in order to determine the average molecular weight and the molecular weight distribution profile. Table II shows that these two polymers have a relatively narrow distribution and that the molecular weight corresponds to 30–50 silicon atoms in each segment.

The thermal stabilities of some cyano-containing organosiloxanes were demonstrated by TG analysis (Fig. 4). Polymers 2 and 3, containing methyltolyl groups, are more stable (*ca.* 270°C) towards weight loss than polymer 1 with bis(tolyl) and methylvinyl group substitution (*ca.* 240°C). A rubber, cross-linked with 5% DCP (and not rinsed), shows a degradation profile which is not significantly different from that of the parent gum. The results obtained by TG analysis were also confirmed by DSC analysis. We conclude that no rearrangement occurred in the gums during heating.

The degradation which begins at temperatures above 250°C represents the start of the total degradation of the polymer. The low-molecular-weight molecules leaving the polymer at 275°C were studied by on-line pyrolysis GC-MS analysis. Volatile products from polymer 60CN-5 can thus be seen in Fig. 5. No detectable amounts of silicon-cyanopropyl cleavage were found, but toluene, possibly from silicon-tolyl, cleavage was detected. It can be noted that, even after heating at 200°C with nitrogen purging, methylene chloride still remains in the polymer. All residual solvent should

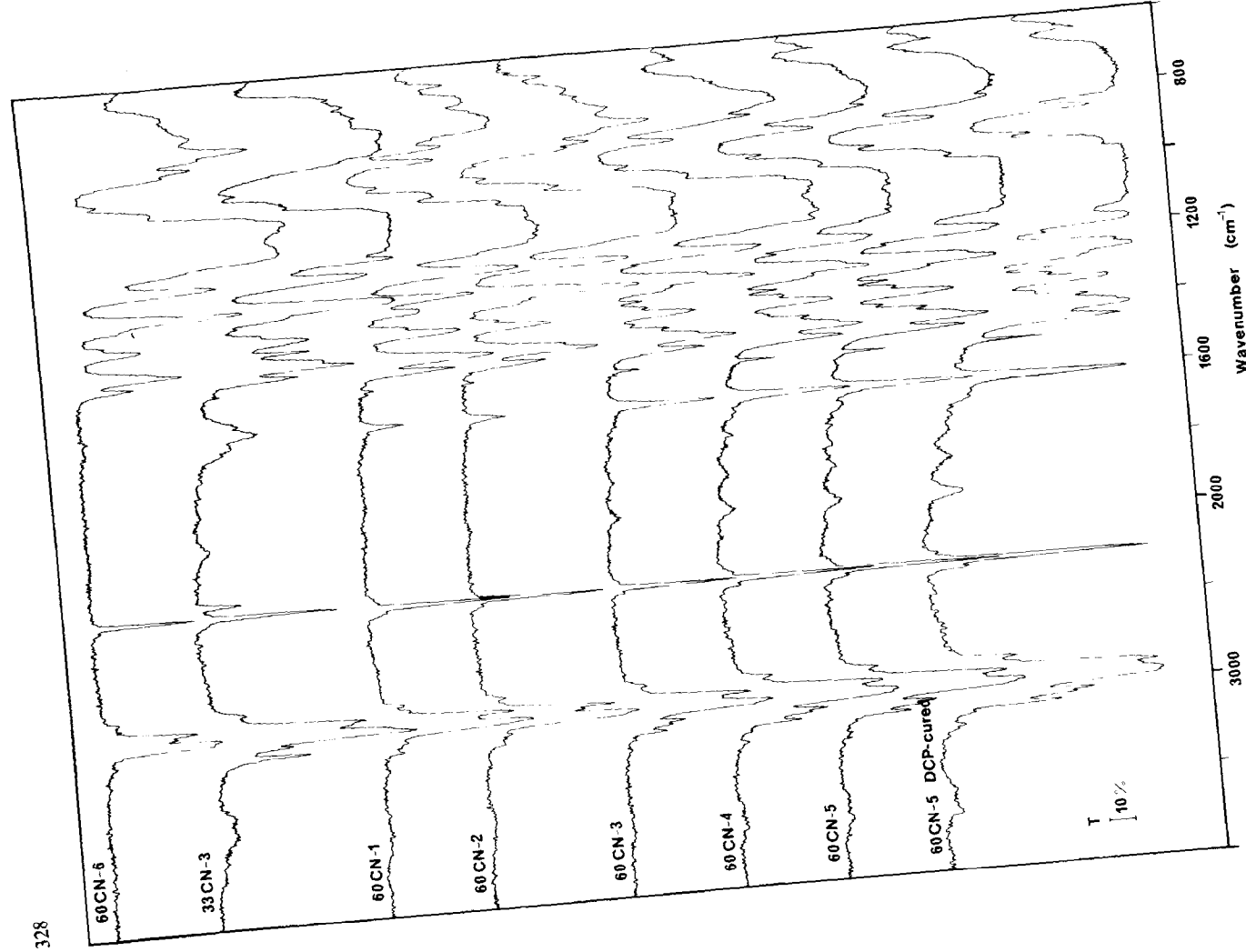


Fig. 2. IR spectra of polysiloxanes containing bis(γ -cyanopropyl) groups. No carboxamide (NH_2 stretches at 3360 and 3470 cm^{-1} and $\text{C}=\text{O}$ stretch at 1680 cm^{-1}) is present in these phases, even after curing with DCP (5% of amount of stationary phase).

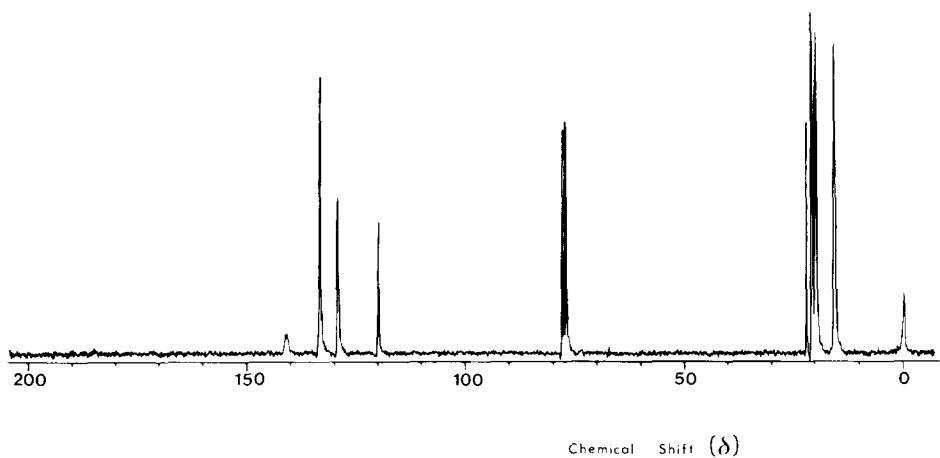


Fig. 3. ¹³C NMR spectrum of 60CN-3 gum, showing that no carboxamide (δ 38.4, CH₂CONH₂; 175.1, CONH₂) is present.

TABLE II
GPC SEPARATIONS

Porous silica microsphere column using tetrahydrofuran as mobile phase and polystyrene as standard.

Stationary phase	Dispersivity	Average mol. weight	Average No. -Si-O- units
60CN-3	1.84	6.971	42
60CN-4	1.89	4.993	30

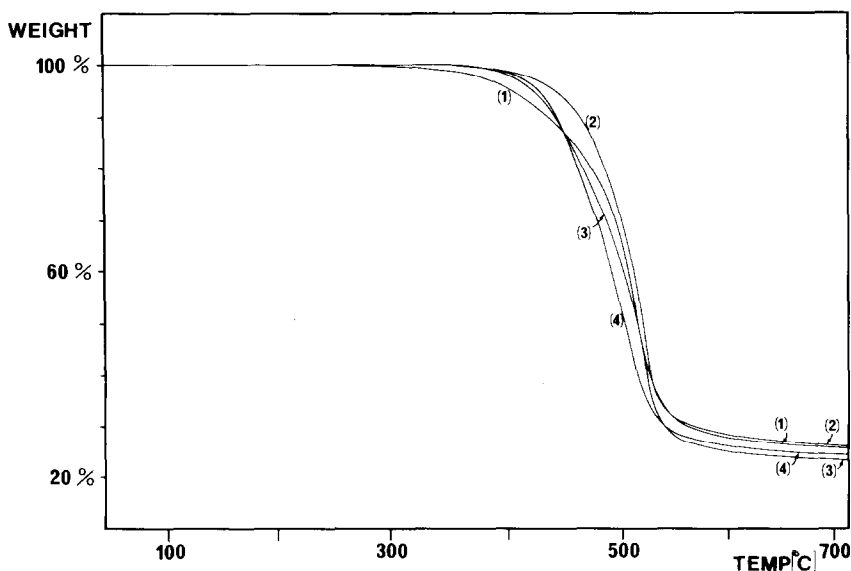


Fig. 4. TG traces for polysiloxanes containing 60% bis(γ -cyanopropyl) groups. Heating rates: 20° min⁻¹; under dynamic nitrogen, 5 ml min⁻¹. Curves: (1) 60CN-2 gum; (2) 60CN-3 gum; (3) 60CN-4 gum; (4) 60CN-4 rubber (DCP-cured).

TABLE III
CHARACTERISTICS OF SOME FUSED-SILICA COLUMNS COATED WITH CYANOSILOXANE RUBBER PHASE

Column No.	Stationary phase	d_f (μm)	Column		Chemical modification	Curing agent	k' (90°C) Naphthalene	HETP (mm)	UTE* (%)	Kováts retention index	
			l (m)	I.D. (mm)						Octanol	Naphthalene
1	33CN-1	0.26	20	0.25	HCl/N ₂ -270°C-5 h/50CN	DCP	19	0.28	82	1394	1563
2	33CN-1	0.28	20	0.25	H ₂ O/N ₂ -260°C-5 h/50CN	ATB	16	0.22	104	1382	1554
3	33CN-1	0.22	19	0.25	HCl/N ₂ -270°C-5 h/50CN	10 Mrad	13	0.26	87	1384	1549
4	33CN-1	0.28	11	0.25	HCl/N ₂ -270°C-5 h/50CN	Ozone	15	0.28	82	1396	1560
5	33CN-2	0.20	15	0.25	HCl/N ₂ -270°C-5 h/100CN	DCP	12	0.35	65	1413	1579
6	33CN-3	0.34	15	0.22	—	DCP	29	0.28	73	1405	1548
7	50CN-1	0.10**	4.5	0.05	HCl/N ₂ -270°C-10 h/50CN	DCP	30	0.13	36	1480	1666
8	50CN-1	0.07	20	0.25	HCl/N ₂ -270°C-5 h/50CN	25 Mrad	3	0.35	56	1487	1667
9	50CN-1	0.12	21	0.25	H ₂ O/N ₂ -260°C-5 h/50CN	ATB	9	0.26	81	1472	1665
10	50CN-1	0.15	10	0.25	—	Ozone	10	0.30	73	1508	1700
11	50CN-1	0.28	49	0.25	HCl/N ₂ -260°C-5 h/50CN	DCP	15	0.29	79	1488	1679
12	60CN-1	0.05	20	0.25	HCl/N ₂ -270°C-10 h/100CN	DCP	2	1.24	18	1543	1783
13	60CN-2	0.13	15	0.22	HCl/N ₂ -270°C-10 h/100CN	ATB	11	0.39	51	1570	1776
14	60CN-3	0.27	20	0.25	HCl/N ₂ -270°C-10 h/100CN	DCP	18	0.30	77	1530	1728
15	60CN-3	0.25	20	0.22	HCl/N ₂ -270°C-10 h/100CN	ATB	22	0.37	55	1529	1732
16	60CN-4	0.15	20	0.25	HCl/N ₂ -270°C-10 h/100CN	DCP	11	0.34	66	1530	1733
17	60CN-5	0.10**	4.5	0.05	HCl/N ₂ -270°C-10 h/100CN	DCP	26	0.17	27	1530	1730
18	60CN-5	0.24	20	0.25	HCl/N ₂ -270°C-10 h/100CN	DCP	9	0.35	63	1527	1729
19	60CN-6	0.16	20	0.22	—	DCP	12	0.31	64	1637	1853
20	60CN-6	0.25	60	0.22	HCl/N ₂ -270°C-5 h/100CN	SiCl ₄ /NH ₃	6	0.27	70	1608	1809
21	75CN-1	0.28	19	0.25	HCl/N ₂ -260°C-5 h/100CN	DCP	15	0.25	91	1601	1830

* UTE = Utilization of theoretical best efficiency.

** Not rinsed.

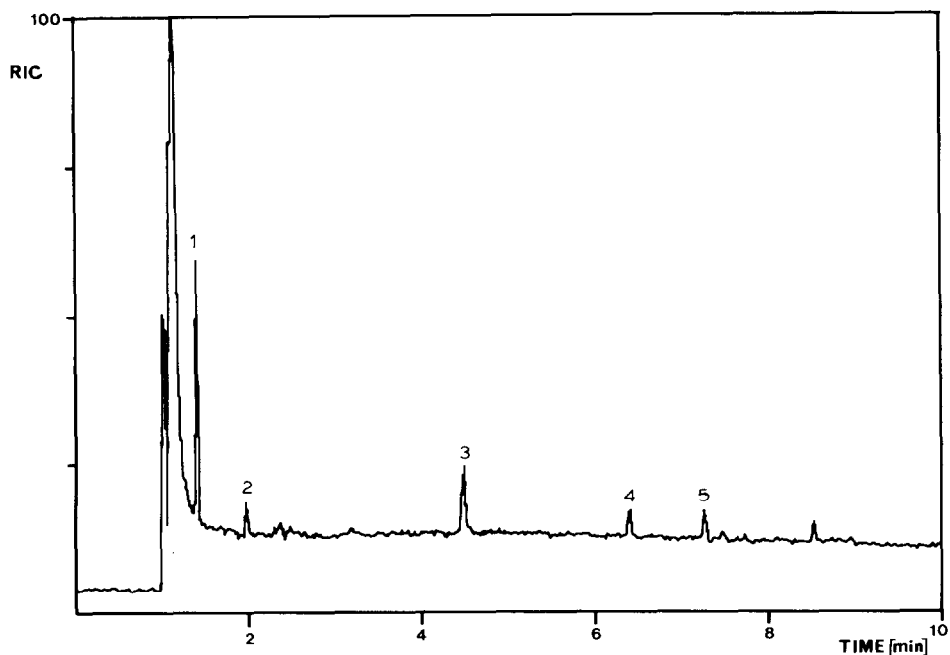


Fig. 5. Pyrolysis GC-MS of a 60CN-5 gum. Peaks: 1 = methylene chloride; 2 = tetrahydrofuran; 3 = toluene; 4 = silane; 5 = disiloxane.

be removed from stationary phases before they are stored in metal-free bottles under an inert atmosphere. The composition of the high-boiling part of the thermal degradation products has been published elsewhere²⁸.

Chromatographic properties

In Table III are summarized the characteristics of some fused-silica columns coated with cyanosiloxane rubber phases. The experimental work had been executed over several years and not all parameters involved were kept constant, *e.g.*, fused-silica capillary tubing material and gas chromatograph.

A pretreatment, including treatment with water or acid at elevated temperatures, followed by rinsing with water-methanol, dehydration and chemical modification at high temperatures, of the columns was performed. The purpose of this is to create a hydroxylated surface receptive for chemical modification with cyclic siloxanes, containing cyano groups. Treatment with HCl at 160°C will give a more neutral surface than would a treatment with water at 375°C. However, the latter results in a somewhat higher efficiency. For dehydration, purging with a slow flow of nitrogen at 260°C during 5 h seems to be optimal. Table III shows that dehydration at 270°C for 10 h resulted in low efficiencies for columns 11-19. The cyclic siloxanes used for chemical modification were found by MS analysis to consist mainly of cyanopropyl(methyl)cyclotetrasiloxane; the content of corresponding tri- and penta-cyclics was *ca.* 15%.

Some batches of fused silica can be successfully coated with polar phases without any pretreatment. However, these capillaries should be thoroughly flushed with dry nitrogen prior to use, as described by Lipsky and McMurray²⁹. All stationary

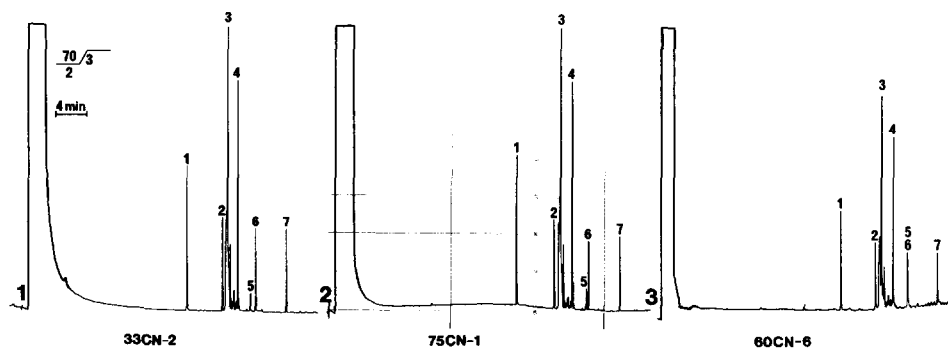


Fig. 6. Gas chromatograms (flame ionization detection) of a fatty acid methyl ester reference mixture, "Complex Cis/Trans Isomer Mix", (Cat. No. 4-5170); Supelco, Bellefonte, PA, U.S.A., showing the selectivity range of some cyano-substituted silicone rubber phases. Fused-silica columns: 1, 33CN-2 rubber (15 m \times 0.25 mm I.D.); 2, 75CN-1 rubber (19 m \times 0.25 mm I.D.); 3, 60CN-6 rubber (20 m \times 0.22 mm I.D.). Peaks: 1 = 16:0; 2 = 18:0; 3 = 18:1 *trans*-4-isomers, 18:1 *cis*- and *trans*-2-isomers and 18:1 *cis*-4-isomers; 4 = 18:2; 5 = 18:3; 6 = 20:0; 7 = 20:1.

phases in Table III are soluble in methylene chloride, and a static coating is thus easily effected. The columns should be thoroughly freed from remaining solvents before the cross-linking is performed.

Curing methods. Different curing agents were used for the *in situ* cross-linking step. Ozone, being an effective radical promoter, is recommended for the cross-linking of non-polar to medium polar (33CN) phases²⁶. With these columns, bleeding was remarkably low. The positive shift in retention index observed for column 10 (50CN-1 phase) is probably due to the introduction of oxygenated groups on the stationary-phase polymer²⁶. Radiation is an attractive method, in theory, for the formation of radicals, one advantage being that no substances are added that can react with the stationary phase. For practical reasons, however, only the 33CN phase could be satisfactorily cross-linked by this method.

Of the azo compounds tested, ATB gave the best results, considering the degree of cross-linking, neutrality and efficiency of the columns. A decrease in efficiency, after ATB treatment of gum phases, indicates that the cross-linking procedure could be improved. DCP was used extensively as a cross-linking agent in this study. When a high concentration of peroxide, *i.e.*, over 3%, is dissolved in the phase for the static coating, a reduced film stability is observed which can affect the efficiency. A room-temperature cross-linking procedure was carried out on column 21 (Table III). Si-O-Si cross-links were thus formed through the action of SiCl₄ on an -OH terminated phase, followed by condensation in an atmosphere of dry ammonia at room temperature.

Column selectivity. Fig. 6 shows the selectivity range for differently substituted stationary phases. Peak 3 contains three groups of isomers. The 18:1-*trans*-4 isomers were eluted at the beginning and the 18:1-*cis*-4 isomers at the end of this group of peaks. An increase in the cyano substitution from 33 to 75% increases $I_N - I_{01}$ (the difference in Kováts indexes) at 90°C from *ca.* 170 to 230 units, the $I_N - I_{01}$ value for the non-polar phase SE-30 being 102 units lower than that for the 33% CN phase.

In Fig. 7, a fatty acid methyl ester standard, PUFA-2, is used to demonstrate

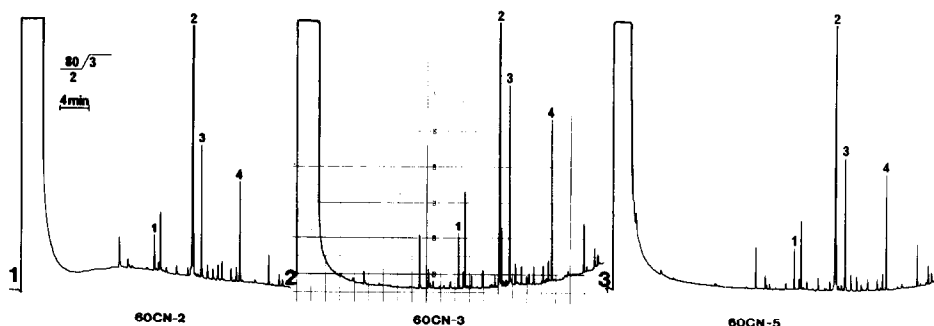


Fig. 7. Gas chromatograms (flame ionization detection) on fused-silica capillary columns, coated with cyanosilicone rubber phases containing 60% cyanopropyl substitution, showing the dependence of selectivity on the different synthetic paths used. Fused-silica columns: 1, 60CN-2 rubber (15 m \times 0.22 mm I.D.); 2, 60CN-3 rubber (20 m \times 0.25 mm I.D.); 3, 60CN-5 rubber (20 m \times 0.25 mm I.D.). Sample: a fatty acid methyl ester standard mixture, PUFA 2 (Supelco). Peaks: 1 = 16:1; 2 = 18:1; 3 = 18:2; 4 = 20:4.

the influence of the synthetic path on the resulting chromatographic properties. The retentions of this sample on these three phases are almost identical. The phase 60CN-3 gives the best separations, *cf.*, the small peaks eluted between peaks 3 and 4. It is evident that, of the synthetic methods tested, reversed basic hydrolysis gives the best results. The columns used in Fig. 9 were also coated with such a phase, synthesized by reversed basic hydrolysis.

Table III shows that the retention indices for octanol and naphthalene on phases 60CN-1 and 60CN-2, having bis(tolyl)methylvinyl substitution, are somewhat higher than on the other phases containing methyltolyl substitution. The efficiencies are comparable for these columns, the low values being a result of excessive dehydration of the capillary tubing in the pretreatment step.

Influence of synthetic path. Some conclusions can be drawn about the influence of the synthetic path on the chromatographic performance of the phases synthesized.

(1) The use of either chloro- or methoxysilanes as starting monomer for the synthesis seems to have no effect on the resulting polymer, if care is taken during the synthetic procedure.

(2) When methyltolyl was replaced by bis(tolyl) plus methylvinyl groups to make cross-linking feasible, improved high temperature stability did not result. In fact, tolyl groups, together with cyano groups, can, in some cases, cause disturbing peak-shaped column bleeding between *ca.* 260 and 270°C.

(3) The polymer prepared through a basic reversed hydrolysis resulted in a stable gum with good chromatographic properties.

(4) A non-hydrolytic cyclization, giving rise to different cyclics with homogeneous substitution in each cyclic, as in phase 60CN-1, resulted in poor chromatographic performance. In the size-exclusion fractionation it could be already seen that the phase was inhomogeneous in structure, a series of low-molecular-weight compounds remaining in the gum. The film formation properties of the gum were poor, and the gum was also difficult to cross-link.

(5) Promising results were achieved when the corresponding substituents were mixed within the cyclics during a non-hydrolytic cyclization. Thus, columns 16 and

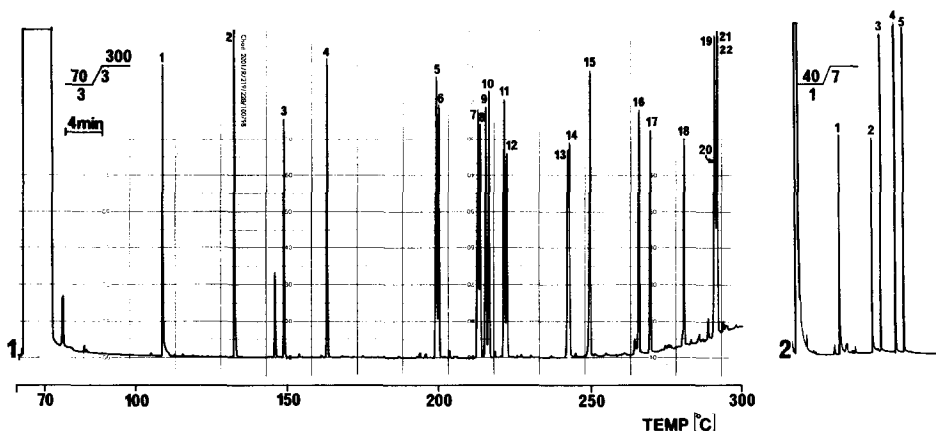


Fig. 8. Gas chromatograms (flame ionization detection) on a fused-silica column (20 m \times 0.22 mm I.D.) coated with silarylene/bis(γ -cyanopropyl)siloxane copolymer (33% CN) rubber phase. Chromatogram 1: a polynuclear aromatic test mixture showing thermal stability. Bleeding at 300°C corresponds to 0.16 pA with a carrier gas flow-rate of 50 cm sec⁻¹. Peaks: 1 = naphthalene; 2 = biphenyl; 3 = acenaphthylene; 4 = fluorene; 5 = phenanthrene; 6 = anthracene; 7 = 2-methylphenanthrene; 8 = 2-methylanthracene; 9 = 1-methylanthracene; 10 = 1-methylphenanthrene; 11 = 9-methylphenanthrene; 12 = phenyl-naphthalene; 13 = 9,10-dimethylanthracene; 14 = fluoranthene; 15 = pyrene; 16 = 1-methylpyrene; 17 = dihydrotetracene; 18 = benzo[*c*]phenanthrene; 19 = benz[*a*]anthracene; 20 = cyclopenta[*c,d*]pyrene; 21 = chrysene; 22 = triphenylene. Chromatogram 2: an amine test mixture, showing adsorption properties, *ca.* 1 ng per peak. Peaks: 1 = octylamine; 2 = decylamine; 3 = dicyclohexylamine; 4 = aniline; 5 = 2,6-dimethylaniline.

18 in Table III exemplify the reproducibility between two batches of gum phase synthesized by this procedure.

(6) When methylvinyl blocks, instead of tolyl groups, are incorporated in the polymer in order to facilitate cross-linking, the resulting columns (19 and 20) show a higher retention index for octanol and naphthalene. Some adsorption of hydrocarbons can result if the cross-linking becomes too dense. 3 mol % of the methylvinylcyclopentasiloxane represents about the maximum tolerable percentage, if good chromatographic properties are to be maintained in the rubber phase.

(7) Column 6 in Table III indicates the successful results achieved by the use of arylene units in the siloxane chain. This stationary phase, 33CN-3, can easily be cross-linked with only 1.5% DCP. The good chromatographic properties of this phase are demonstrated in Fig. 8, showing a high-temperature chromatogram of a PNA (polynuclear aromatic) test solution and an amine test on the phase coated on a non-deactivated fused-silica capillary tubing. A silarylene/methylphenylsiloxane stationary phase has been described elsewhere³⁰.

Column 21 in Table III is coated with a 75CN-1 phase. This phase was used in earlier work⁵; then it possessed a somewhat higher polarity than obtained here (I_{01} was 1647, and is now 1601). This difference may be explained by the fact that the 75CN-1 phase has now been cleaned by size exclusion chromatography to remove all material of MW lower than 1000. Aging of a column can affect the retention performance. After rinsing a rubber column with a solvent, it takes some time before all solvent is removed from the phase. The column performance is impaired under these conditions.

TABLE IV

CHARACTERISTICS OF FUSED-SILICA COLUMNS, COATED WITH 50CN-1 RUBBER

Column No.	Stationary phase	Length (m)	I.D. (mm)	d_f (μm)	Amount of phase (μg)	Flow-rate (ml/min)	β^*
1	50CN-1	4.5	0.05	0.10	0.07	0.06	125
2	50CN-1	20	0.25	0.20	3.1	1.5	312

* β = Phase ratio.

Narrow-bore columns. Some columns ($4.5 \text{ m} \times 50 \mu\text{m}$ I.D.) were coated with cyanosiloxane rubber phases. A comparison between some characteristics of these columns and those of a 0.25 mm I.D. column are given in Table IV.

The low amount of phase present in these thin columns will result in reduced bleeding characteristics as compared with ordinary capillary columns. At the same time, the elution temperature for a sample on column 1, in Table IV, will be *ca.* 40°C below the elution temperature of the same sample on column 2 with the same temperature program. High-speed analysis can be performed on these small-diameter columns^{31,32}.

Fig. 9 shows the elution of PUFA-2 on a $50 \mu\text{m}$ I.D. column. The analysis of a fatty acid methyl ester standard solution was thus completed after 6 min instead of 30 min on a conventional capillary column. These columns were prepared ac-

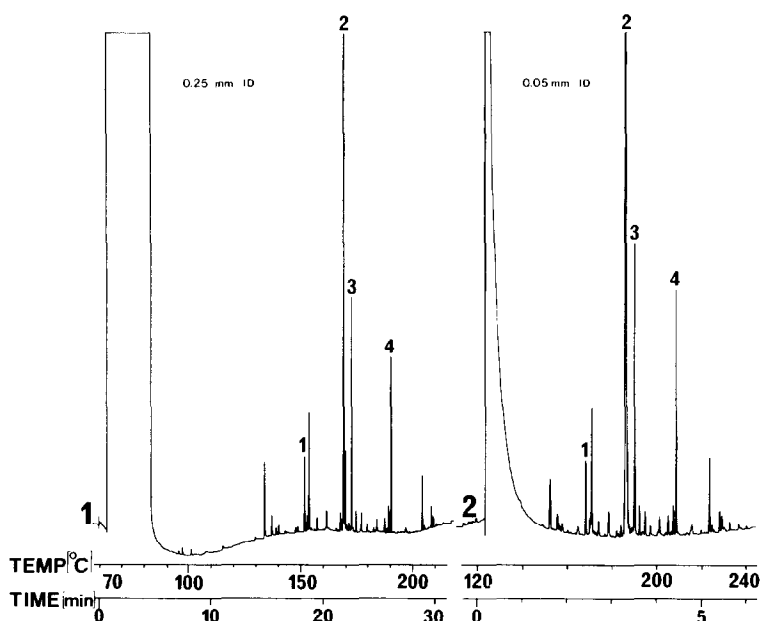


Fig. 9. Gas chromatograms (flame ionization detection) of a fatty acid methyl ester mixture "PUFA 2" (Supelco) on two different fused-silica columns: 1, $21 \text{ m} \times 0.25 \text{ mm}$ I.D., d_f $0.12 \mu\text{m}$, analysis time 30 min; 2, $4.5 \text{ m} \times 0.05 \text{ mm}$ I.D., d_f $0.10 \mu\text{m}$, analysis time 6 min. Peaks: 1 = 16:1; 2 = 18:1; 3 = 18:2; 4 = 20:4.

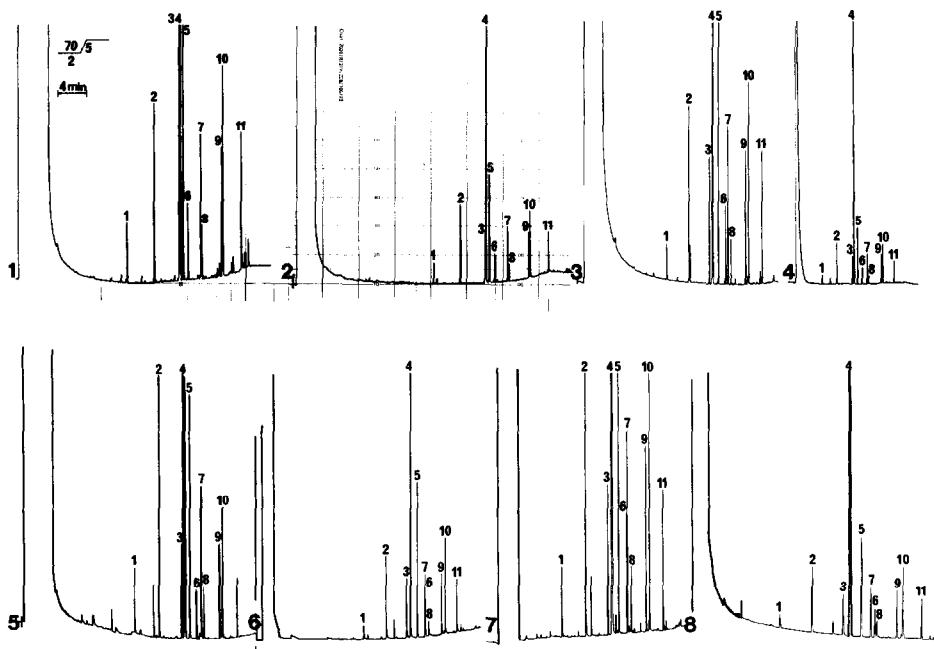


Fig. 10. Gas chromatograms of a fatty acid methyl ester reference mixture rapeseed oil (Supelco) on different fused-silica columns, coated with cyano-rubber phases. Columns: 1, 33CN-1; 2, 33CN-3; 3, 33CN-2; 4, 50CN-1; 5, 60CN-5; 6, 60CN-6; 7, 75CN-1; 8, 88CN (kindly donated by Dr. M. Lee). Peaks: 1 = 14:0; 2 = 16:0; 3 = 18:0; 4 = 18:1; 5 = 18:2; 6 = 18:3; 7 = 20:0; 8 = 20:1; 9 = 22:0; 10 = 22:1; 11 = 24:0. Chromatogram 4 was programmed at $7^{\circ}\text{C min}^{-1}$ from 110°C . The column ($4.5\text{ m} \times 50\ \mu\text{m}$ I.D.) had a film thickness of $0.10\ \mu\text{m}$.

cording to the same procedure as the conventional columns, and were used in a gas chromatograph without any instrumental modifications. A make-up flow to the detector was used, as recommended by Schutjes *et al.*³², in order to increase the detector sensitivity.

Fatty acid methyl ester (FAME) applications. A polar column is required for the separation of *cis/trans* isomers of fatty acid methyl esters, and cyanosilicones have been extensively used for such separations^{33,34}. For the separation of samples containing positional and geometrical isomers, polar columns with high separation efficiencies are needed. It has been one of the objects of this work to combine polarity and efficiency; our success in this respect may be determined by the analysis of FAME. Further, we strove for high thermal stability, which may be demonstrated by the separation of diglycerides. There is much interest in the analysis of FAME, and during recent years we have assisted several laboratories in Sweden with their analyses. Some of the applications thus performed are shown in Figs. 10–13.

The separation of a rapeseed oil standard on eight different columns is shown in Fig. 10. First, it may be seen that the use of vinyl blocks for curing (chromatograms 3 and 6) gives somewhat higher polarity than when tolyl groups are used (chromatograms 1 and 5). Further, incorporation of arylene gives a polarity similar to tolyl substitution. Secondly, if overlap of the 18:3 and 20:0 isomers is undesirable,

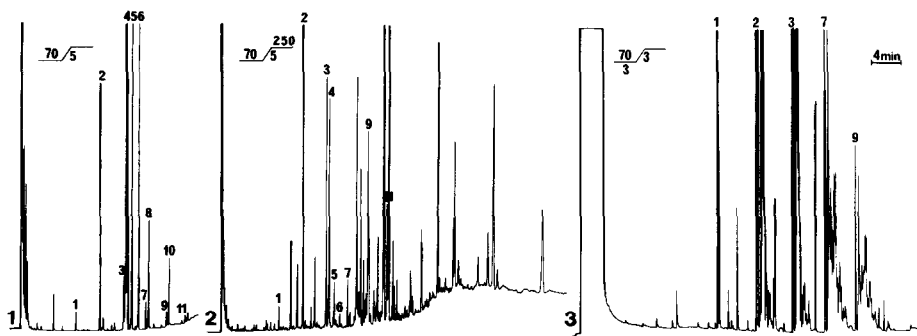


Fig. 11. Gas chromatograms (flame ionization detection) of fatty acid methyl esters of different origins. Chromatogram 1, Column: 50CN-1 rubber (12 m \times 0.25 mm I.D.), d_f 0.20 μ m; sample, methylated rapeseed oil LOBRA. Chromatogram 2, Column: 50CN-1 rubber (10 m \times 0.30 mm I.D.), d_f 0.15 μ m; sample, methylated fatty acids from paper and glue resin extract. Chromatogram 3, Column: 75CN-1 rubber (20 m \times 0.25 mm I.D.), d_f 0.28 μ m; sample, methylated hydrogenated fish oil Menhaden, 40°C. Peaks: 1 = 14:0; 2 = 16:0; 3 = 18:0; 4 = 18:1; 5 = 18:2; 6 = 18:3; 7 = 20:0; 8 = 20:1; 9 = 22:0; 10 = 22:1; 11 = 24:0.

the maximum polarity is achieved for 60% cyanopropyl and 20% tolyl substitution (chromatogram 5). Thirdly, analysis of rapeseed oil had been performed earlier on the phase used in chromatogram 7⁵. In that analysis, the 18:3 isomer was eluted between 20:0 and 20:1; now it is eluted together with 20:0. The difference may be explained by the fact that the phase has now been purified by GPC. The polarity was thus somewhat lowered. Furthermore, much more efficient columns can be prepared when the phase has been purified by GPC. The HETP was⁵ 0.34 mm for naphthalene at 90°C, but after GPC purification, it was lowered to 0.25 mm under the same conditions. Supelco reported³⁵ the separation of the isomers 18:1 and 18:2 on their SP-2330 phase. It can be assumed that this separation is due to the presence of carboxamide groups in the stationary phase. The presence of such groups in SP-2330

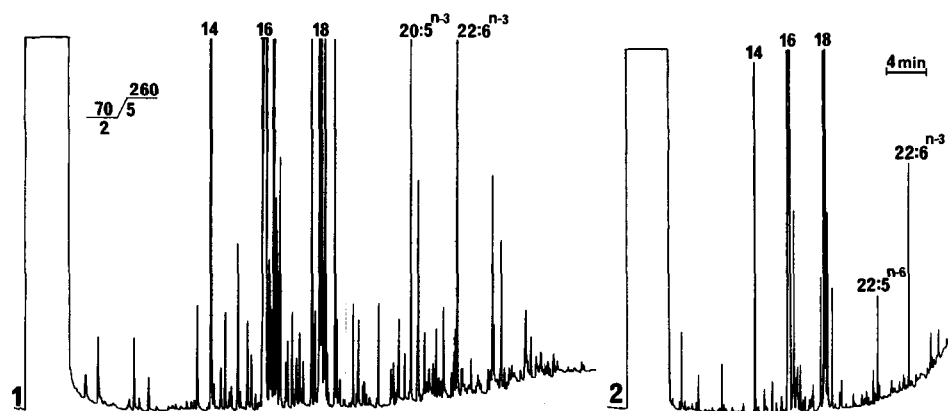


Fig. 12. Gas chromatograms (flame ionization detection) of (1) fatty acid methyl esters from a herring liver extract, on a 20-m column coated with 75CN-1 rubber, and (2) from a biological testis standard mixture, on a 20-m column coated with 50CN-1 rubber.

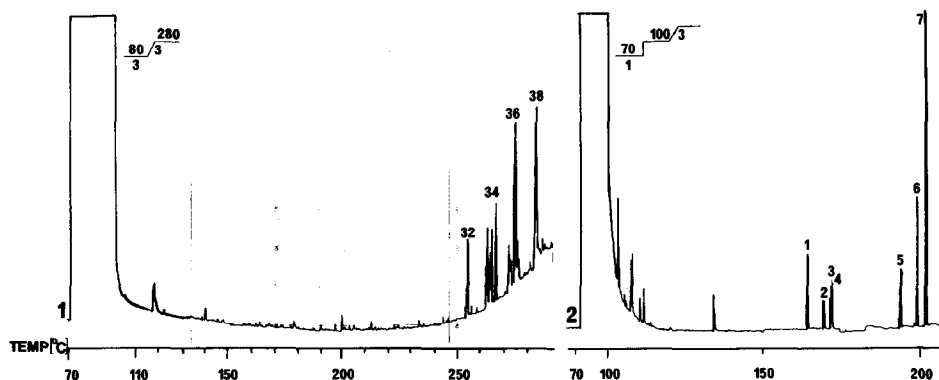


Fig. 13. (1) Gas chromatogram (flame ionization detection) of a methylated diglyceride sample. Column: 4.5 m \times 0.05 mm I.D., d_f 0.10 μ m, 60CN-5 rubber. Peaks: diglycerides of the type 1,2-diacyl-*sn*-glycerol-3-trimethylsilyl ether with a total of 32–38 carbons in the substituted fatty acid chains. (2) Gas chromatogram (flame ionization detection) of a synthetic pheromone sample (red-banded leafroller moth). Column: 50-m fused silica, pretreated with HCl and 50CN-cyclic siloxane deactivation, coated with a 50CN-1 rubber phase (DCP-cured). Peaks: 1 = 12:Ac; 2 = E9-12:Ac; 3 = Z9-12:Ac; 4 = 11-12:Ac; 5 = 14:Ac; 6 = E11-14:Ac; 7 = Z11-14:Ac.

was recently demonstrated by Jones *et al.*⁸. Fourthly, the capillaries were high-temperature silylated with cyanopropylcyclorosiloxane. Such treatment is necessary in order to achieve deactivation and wettability by the stationary phases. When comparing the polarity of columns coated with 88CN on non-pretreated fused silica⁸ and on fused silica that has been high-temperature silanized (chromatogram 8), it is seen that on non-pretreated columns, 18:3 is eluted before 20:0; in chromatogram 8 the elution order of these components is reversed.

Fig. 11, 1 shows the separation of a rapeseed oil (LOBRA) having a low content of erucic acid. The analysis of fatty acids is of great importance in the pulp and paper industry³⁶. Fig. 11, 2 shows the separation of methylated fatty acids from a paper and glue extract. Fig. 11, 3 shows the separation of methylated, hydrogenated fish oil (Menhaden oil).

Fig. 12 shows two reference test mixtures containing the fatty acid methyl esters 20:5ⁿ⁻³, 22:6ⁿ⁻³ and 22:5ⁿ⁻⁶, which are of interest in biomedical research.

Fig. 13, 1 shows the separation of methylated diglycerides from rat pancreas on a narrow-bore column. The stationary phase used, 60CN-5, normally shows bleeding above 250°C, but due to the low amount of phase in the narrow-bore column, temperature programming could be continued to 280°C without unacceptable column bleeding. The separation of a synthetic pheromone mixture is shown in Fig. 13, 2. The pheromones Z9-12:Ac and 11-12:Ac (peaks 3 and 4) have not previously been separated³⁷.

CONCLUSIONS

In conclusion, this work demonstrates the influence of the synthetic paths used for the synthesis of stationary gum phases on the chromatographic performance of the resulting columns. The best results were obtained when reversed basic hydrolysis was used.

Different possibilities to facilitate cross-linking of polar organosiloxane gums were evaluated. Thus, tolyl groups facilitate cross-linking, the resulting gum having very good properties, although some bleeding can be a problem in high-temperature analysis, *i.e.*, over 260°C. Methylvinyl groups can be successfully used if short blocks of at least five Si-O units are being utilized, the bleeding being somewhat lower than for the tolyl-containing phases. A promising approach to facilitate cross-linking and at the same time to gain high-temperature stability is the incorporation of arylene units in the siloxane chain, forming a bis(γ -cyanopropyl)methylsilylenosiloxane block copolymer.

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