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ROLE OF SURFACE GROUPS IN AFFECTING THE CHROMATOGRAPHIC PERFORMANCE OF CERTAIN TYPES OF FUSED-SILICA GLASS CAPILLARY COLUMN

III. THE DEACTIVATION AND COATING OF CERTAIN SPECIALLY PREPARED HIGH-MOLECULAR-WEIGHT, HIGH-VISCOSITY NON-POLAR AND POLAR STATIONARY PHASES ON UNTREATED FUSED-SILICA SURFACES IN A SINGLE STEP

S. R. LIPSKY* and W. J. McMURRAY

Section of Physical Sciences, Department of Laboratory Medicine, Yale University School of Medicine, New Haven, CT 06510 (U.S.A.)

SUMMARY

High-molecular-weight, high-viscosity, non-polar, silanol-terminated polydimethylsiloxane polymers with and without phenyl substitution when applied in a single step to untreated fused-silica glass capillary tubing efficiently deactivated and wetted these surfaces. Upon heating, there is evidence that hydrogen bonding occurred between the silanol moieties of the polymer and those of the fused-silica surface. This formed a covalent linkage between the polymer and the glass. Concomitant condensation of the polymer occurs, effecting crosslinking of the $-\text{Si}-\text{O}-\text{Si}-$ type.

Successful single-step deactivation and uniform wetting was also noted with a wide variety of high-molecular-weight, high-viscosity, polar cyanopropyl silicone polymers with vinyl or tolyl groups. In many instances, however, difficulties were encountered in the cross-linking of these polymers in the presence of free radical generators.

Under certain experimental conditions, the mechanisms that give rise to the surface deactivation of untreated fused-silica glass in the presence of certain other non-polar and polar polymers with various chemical compositions are unknown at this time.

INTRODUCTION

In a previous paper from this laboratory¹, a preliminary investigation demonstrated the possibility of covalently bonding specially prepared non-polar, high-molecular-weight, viscous, silanol-terminated polysiloxane stationary phases to the surface silanol groups of *untreated* fused-silica glass capillary tubing and simultaneously cross-linking the polymer by condensation. In certain instances, it was found that this procedure could be readily carried out in a single step by a simple and effective

heat treatment. Although slight activity was noted in some of these early attempts, nonetheless we were soon able to produce a stable, non-extractable film on a neutral surface.

In this same publication¹, chromatograms were also presented which depicted the very successful single-step *deactivation* and uniform *coating* of an untreated fused-silica glass capillary column with

(a) a *non-polar* high-molecular-weight, high-viscosity methyl 20% phenyl polysiloxane polymer vinyl-terminated and

(b) a *polar* high-molecular-weight, high-viscosity vinyl-terminated methyl polysiloxane with 75% cyanopropyl-methyl substitution.

In both instances, it should be noted however, that effective cross-linking to a high-yield non-extractable immobilized layer² required an additional manipulation—one that was readily carried out by the simple exposure of the chromatographically tested column to a dynamic flow system³ containing the free radical generator, azo-*tert.*-butane⁴. Based on these early promising results, it appeared that additional studies were warranted here in an effort to achieve certain highly desirable goals. These were:

(1) To produce in a single step, a simple, fast, reliable and reproducible method for the complete *deactivation* of the slightly acidic untreated surface of the fused-silica glass tubing as well as the easy coating, wetting, and homogeneous spreading of a non-polar polymeric film throughout the capillary column thereby providing excellent efficiency and film stability.

(2) To produce the effective cross-linking and immobilization of the polymer with heat alone or heat combined with an innocuous catalyst present in the coating solution thereby avoiding the use of:

(a) Certain cross-linking agents such as peroxides which can give rise to undesirable by-products³ which are difficult to extract from the immobilized layer

(b) Vinyl and tolyl substituents in the polymer which facilitate cross-linking but on occasion, give rise to some alterations in the McReynold's constants^{5,6}.

It was thought that information gleaned from these studies on deactivation, wetting, cross-linking and immobilization would also be valuable in attempting to extend these concepts to the application of the highly polar silicone phases containing different cyanopropyl substituents and terminal groups to similar glass surfaces.

EXPERIMENTAL

Untreated fused-silica glass capillary columns were purged with nitrogen at room temperature before use. The purging ceased when all remnants of hydrogen chloride normally found in recently drawn capillary tubing were removed from the coil. This was determined by the placing of a piece of pH paper at the end of the column to monitor the exiting of the volatile acid. For a 25-m column, all traces of hydrogen chloride disappeared in *ca.* 5 min.

The non-polar silanol-terminated polydimethylsiloxane polymers with and without phenyl substitution were made by slight modification of the methods described by Patnode and Wilcock⁷, Madani *et al.*^{8,9} and Buijten *et al.*¹⁰. The non-polar vinyl-terminated methyl phenyl polysiloxane polymers were made by techniques similar to those used by Peaden *et al.*¹¹ and Buijten *et al.*¹⁰, the polar polymers

containing cyanopropyl functionality were prepared by slight alterations of the methods described by Markides *et al.*¹². The final purified products were generally high-molecular-weight, high-viscosity¹³ polymers which exhibited good solubility in pentane and/or methylene chloride. The silanol-terminated polymers were partially cross-linked by heat before use.

Solutions of the polymers were applied to the nitrogen-purged untreated fused-silica glass capillary tubing by either the dynamic or static technique. With reference to the former, concentrations up to 30% in methylene chloride were forced through the capillary tubing with nitrogen by means of a mercury plug (2 cm/sec). Concentrations of 0.3–1.2% in pentane or methylene chloride were used for static coating. Following the completion of either step, traces of solvent were removed by gently purging the fused-silica tubing with nitrogen for 2–3 h at 60°C. With nitrogen still flowing, the non-polar capillary coils were then allowed to cool to room temperature. The ends were placed under vacuum for 30 min and then carefully sealed. The temperature of the non-polar capillary columns was then slowly increased at the rate of 2–4°C/min to 370°C where it remained for 5–15 h. After cooling, the seals were broken and the column was again purged with nitrogen for 60 min. At this point, those columns containing certain phases which exhibited some degree of cross-linking by heat were tested gas chromatographically after conditioning and then rinsed with methylene chloride and pentane. After traces of the solvents were removed by gentle purging with nitrogen, the columns were conditioned and retested with solutions of non-polar and polar test mixtures (0.2–0.04%).

Azo-*tert.*-butane⁴ was used as a free radical generator for cross-linking those polymers that contained vinyl and tolyl substituents. On occasion, an amine, tris-(dimethylamino)methylsilane, was employed along with heat to augment the condensation of silanol-terminated polymers. After the successful chromatographic testing of the non-vulcanized polymeric film, cross-linking was accomplished by using a simple, continuous flow technique³. The vapors of azo-*tert.*-butane (or where appropriate, the trifunctional amine) from a pressurized vial was carried to the column positioned in an oven at 60°C—in a slow, continuous stream of nitrogen for 30 min. The ends of the column were then sealed and the column was slowly programmed to 260°C where it remained for 60 min. The column was then cooled, the seals were broken and the cross-linked layer was washed with methylene chloride and pentane. Traces of solvents were removed by purging with nitrogen. The columns were then conditioned and the capacity factors (k') were compared before and after cross-linking.

RESULTS AND DISCUSSION

It is now well known that the surfaces of various batches of untreated high purity fused-silica glass capillary tubing show enormous variations in activity. This effect may be due not only to the differences in silanol content but also to differences in the amount of unreacted SiCl_4 present in the various performs used in the drawing of the narrow-bore tubing at high temperatures (above 2000°C). In the presence of air and moisture, variable amounts of SiCl_4 are converted into hydrogen chloride gas, which clings to the inner surfaces of the capillary tubing unless preferentially removed by purging with nitrogen. It has been our experience that undisciplined

washing of the untreated surface with solvents prior to the application of deactivating agents or solutions of polymer, tends to make surface deactivating procedures somewhat more difficult to carry out. The same holds true for pre-treatment with aqueous hydrochloric acid and heat. Hydrogen chloride at 350°C⁶ or hydrochloric acid per se at 140°C¹² has no demonstrable effect, other than cleansing, on the fused-silica surface. The water present in the latter instance, however, certainly may substantially increase the number of silanol groups on the surface and increase the reaction between these groups and appropriate groups present in a variety of "deactivating" agents. However, in our hands, this reaction must be very carefully controlled in order to obtain reproducible results. Under these circumstances, we find it is much easier to cope directly with the relatively few silanol moieties on the untreated surface.

Figs. 1 and 2 depict the results obtained when non-polar high-molecular-weight, high-viscosity, silanol-terminated methyl polysiloxane and methyl 5% phenyl

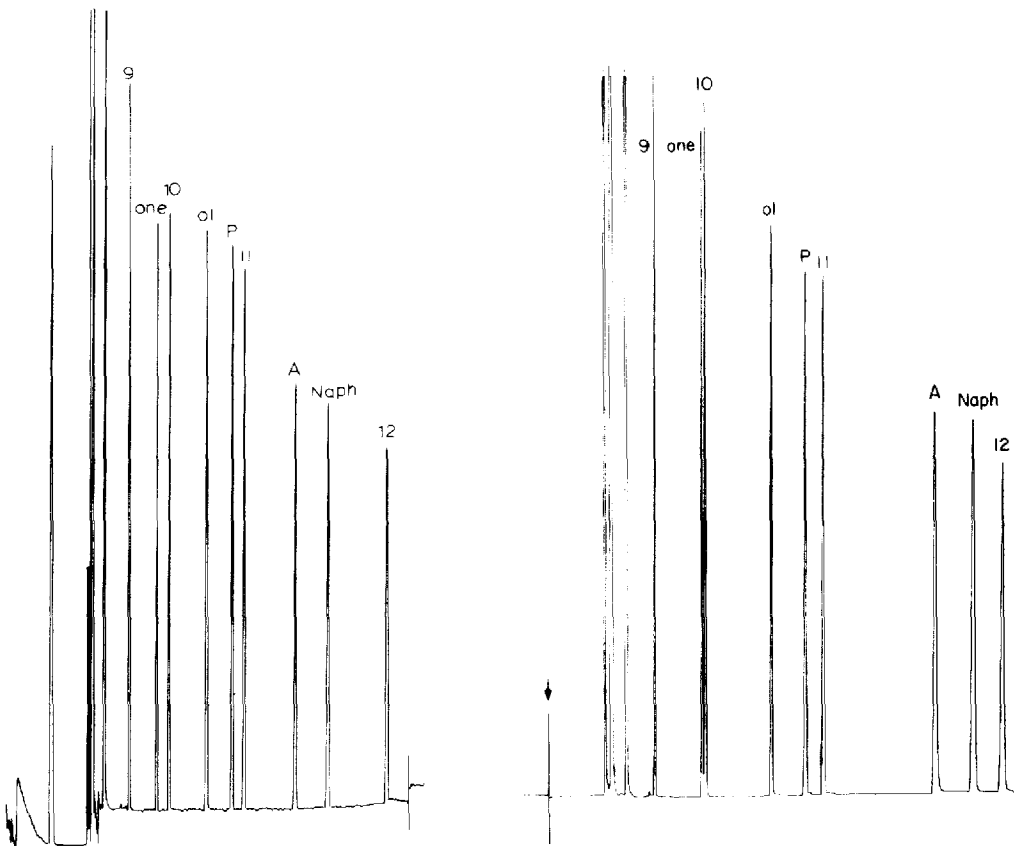


Fig. 1. Analysis of a non-polar test mixture on a fused-silica capillary column (25 m \times 0.25 mm) containing silanol-terminated polydimethyl siloxane coated onto the untreated glass surface. Temperature, 100°C; pressure, 13 p.s.i. hydrogen; chart speed, 60 cm/h. Peaks: 9 12 = C₉ C₁₂ hydrocarbons, one = 2-octanone, ol = 1-octanol, P = 2,6-dimethylphenol, A = 2,4-dimethylaniline, Naph = naphthalene.

Fig. 2. Analysis of a non-polar test mixture on a fused-silica capillary column containing silanol-terminated methyl 5% phenyl polysiloxane coated onto the untreated glass surface. Column dimensions and conditions as in Fig. 1, except pressure: 16 p.s.i. hydrogen. Peaks as in Fig. 1.

polysiloxane partially cross-linked polymers were applied directly to the untreated surface of the fused-silica capillary tubing and were further cross-linked by condensation by heating (with or without an amine catalyst). Several things are of interest here. These polymers readily deactivated the surface. They also readily wetted the surface by distributing themselves as a homogeneous film throughout the length of the column, giving rise to efficiencies of 3000 plates per meter or more. They were stable to above 300°C. Following extraction with methylene chloride and/or pentane, 85-95% of the film appeared to be cross-linked. If these particular polymers were not partially gumified prior to coating, only 50-60% of the condensed film was immobilized.

From these results, it is reasonable to conclude that in the presence of heat, two important reactions have taken place:

(1) Hydrogen bonding was established between the silanol moieties of the polymer and those of the untreated fused-silica surface. This formed a covalent linkage between the polymer and the glass. When the coating was properly carried out, this step provided one with a completely deactivated surface and the low intermolecular forces normally present in films of high-molecular-weight, high-viscosity polydimethylsiloxanes present here permitted the polymer to wet the surface uniformly.

(2) Concomitantly, in the presence of heat and a trace of moisture, condensation probably occurs between the remaining silanol groups of the polymer effecting a degree of cross-linking of the $-\text{Si}-\text{O}-\text{Si}-$ type, in contrast to the $-\text{Si}-\text{C}-\text{C}-\text{Si}-$ linkage noted when vulcanization is brought about by the use of free-radical generators. This results in the formation of an immobilized polymeric layer (and all of its associated chromatographic virtues) which in this instance at least, is also tenaciously bonded to the surface of the fused-silica tubing.

The single step method for bonding and cross-linking the silanol-terminated non-polar polysiloxane polymers was effectively carried out when either the dynamic or static technique was used for the application of the polymer to the untreated fused-silica surface. Depending upon the concentrations of the coating solutions, film thicknesses from 0.10 to 0.75 μm were readily obtained. On occasion, a column was produced that showed early signs of a slightly acid surface (*i.e.* a diminished peak and/or tailing peak representing dimethylaniline). This effect invariably disappeared when the column was resealed and heated to 350°C for 5 h followed by additional solvent rinsing with methylene chloride and pentane.

Others have reported this type of surface bonding readily occurring on silica particles¹⁴⁻¹⁶. However, Madani *et al.*^{8,9} were amongst the first to recognize the possibility of covalently bonding a specially prepared silanol-terminated non-polar polydimethyl siloxane (with and without phenyl substitution) to a borosilicate glass surface as well as simultaneously rendering the polymers non-extractable by cross-linking by condensation with heat. Several differences exist between their study and that from this laboratory. First, they used Pyrex glass treated with hydrogen chloride, in order to supposedly provide additional hydroxyl groups accessible to heat condensation. Second, chromatograms depicting the analysis of appropriate test mixtures which would indicate the extent of deactivation of the glass surface were not presented. Third, no specific changes in the chromatographic properties of the columns were reported before and after solvent extraction, presumably indicating complete cross-linking although k' values were not given here.

Recently, Verzele *et al.*⁶ also immobilized a silanol-terminated methyl 50% phenyl silicone polymer on fused-silica glass by heat curing. However, they pre-treated their fused-silica columns by exposure to hydrogen chloride at 350°C and then "precoated" the surface with a silanol-terminated liquid silicone prepolymer. The column was then sealed and heated to 350°C in order to effectively deactivate the surface. The capillary coil, after solvent rinsing, was then coated a second time with a viscous, partially gumified silanol-terminated methyl 50% phenyl siloxane polymer which was conveniently immobilized by heat curing. Under these circumstances, well deactivated columns containing completely cross-linked layers which also showed well defined selectivity and polarity were obtained. They were stable to 280°C and had a chromatographic efficiency of 80%.

While the aforementioned reactions appear to be a logical explanation for what transpires when a non-polar silanol terminated polysiloxane is employed, it does not readily explain the mechanisms at work when excellent results were obtained¹ when a vinyl-terminated high-molecular-weight high-viscosity methyl 20% phenyl polysiloxane was directly coated onto two different untreated fused-silica capillary coils (one 25 m and one 100 m length). Since this polymer contained vinyl groups, after chromatographically testing the column, cross-linking was readily effected by treatment with azo-*tert.*-butane. Under these circumstances, columns were produced which exhibited very good deactivation as well as wetting characteristics which give rise to high column efficiencies. When exposed to free radical generators, cross-linking readily occurred and after solvent rinsing, 85-90% of the polymeric layer was immobilized.

Obviously, covalent bonding of the phase² to the fused-silica surface could not occur under the conditions of this particular experiment. No "precoating" of surface was used here. Yet deactivation of the tubing, uniform wetting of the surface, cross-linking and almost complete immobilization of the polymeric layer was noted. The precise mechanism by which this non-polar, selective phase deactivates the surface is unknown at this time. The same may be said about certain mechanisms involved when properly prepared high-molecular weight, high-viscosity, *polar* phases containing various degrees of cyanopropyl substitution invariably gave rise to well deactivated surfaces when coated directly onto untreated fused-silica glass tubing. It should be noted, however, that certain difficulties that ensued here with the cross-linking and immobilization on occasion were due to the presence of large amounts of the bis-cyanopropyl moiety giving rise to steric effects which tended to hinder vulcanization.

The gas chromatographic analyses of a polar test mixture obtained from fused silica glass capillary columns coated with a wide variety of different specially prepared experimental cyanopropyl silicane phases are noted in Figs. 3-10. Table I depicts the relationship of the chemical composition of the polymeric phases to order of elution of certain components of the mixture from the columns.

Columns containing phases which have a preponderance of the bis-cyanopropyl moiety are very polar, and accordingly cause the hydrocarbons to emerge more rapidly from the column (Fig. 3 and Table I, A and B). This effect was also noted¹⁷ with the commercial phases OV-275 (Ohio Valley) and SP 2340 (Supelco) when these materials were applied to soft glass capillary columns whose surfaces contained a sodium chloride matrix (via hydrogen chloride treatment). Owing to the relatively

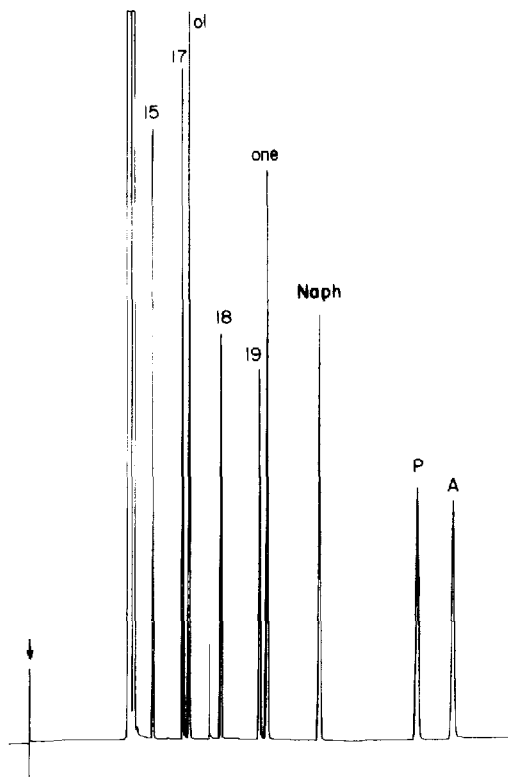


Fig. 3. Analysis of a polar test mixture on a fused-silica capillary column (25 m \times 0.25 mm) containing a cyanosilicone polymer (80% bis-cyanopropyl, 15% methyl, 5% vinyl) coated onto the untreated glass surface. Temperature, 110°C; pressure, 14 p.s.i. hydrogen; chart speed, 120 cm/h. Peaks as in Fig. 1; 15-19 = C₁₅-C₁₉ hydrocarbons, one = cyclooctanone.

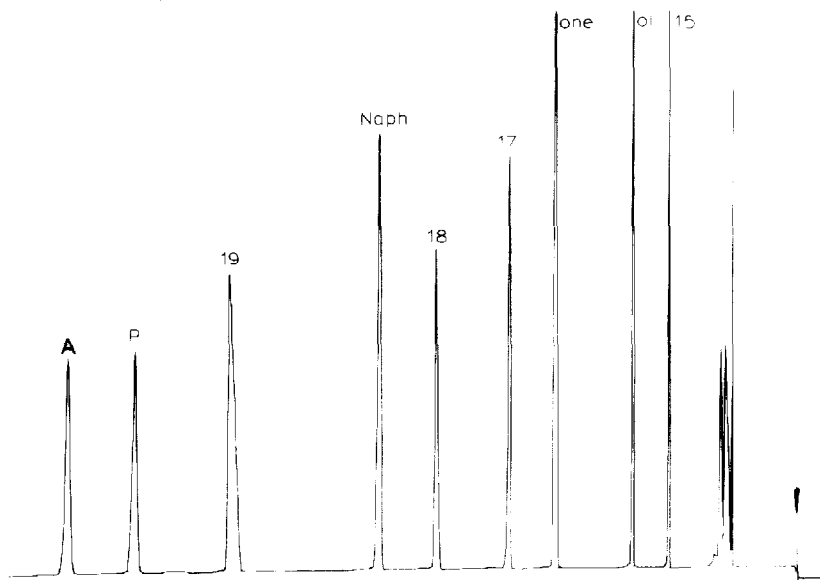


Fig. 4. Analysis of a polar test mixture on a fused-silica capillary column containing a cyanosilicone polymer (85% bis-cyanopropyl, 13% *p*-tolyl, 2% other) coated onto the untreated glass surface. Column dimensions and conditions as in Fig. 3, except pressure: 15 p.s.i. hydrogen. Number of plates per meter for 2,4-dimethylaniline: 4330. Peaks as in Fig. 3.

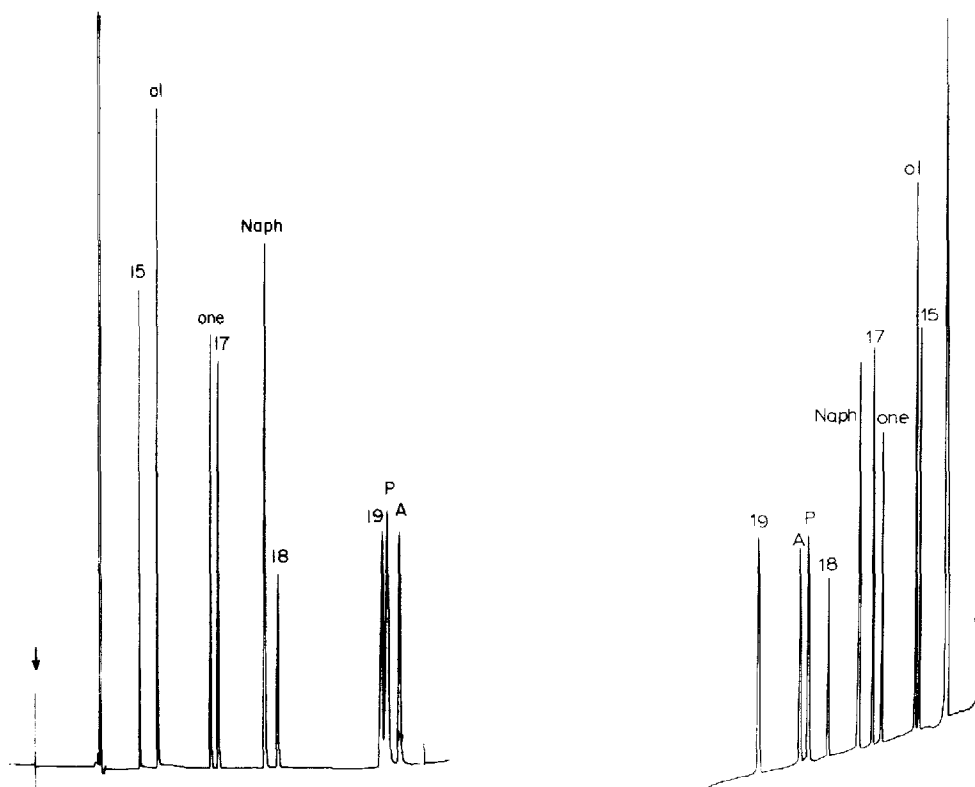


Fig. 5. Analysis of a polar test mixture on a fused-silica capillary column (25 m \times 0.25 mm) containing a cyanosilicone polymer (95% cyanopropyl methyl, 5% vinyl) coated onto the untreated glass surface. Temperature, 120°C; pressure, 14 p.s.i. hydrogen; chart speed, 76 cm/h. Peaks as in Fig. 3.

Fig. 6. Analysis of a polar test mixture on a fused-silica capillary column containing a cyanosilicone polymer (85% cyanopropyl methyl, 10% diphenyl, 5% methyl vinyl) coated onto the untreated glass surface. Column dimensions and conditions as in Fig. 3, except chart speed: 60 cm/h. Peaks as in Fig. 3.

TABLE I

ORDER OF ELUTION OF A POLAR TEST MIXTURE ON A VARIETY OF DIFFERENT CYANOSILICONE STATIONARY PHASES*

(A)	(B)	(C)	(D)
85% <i>bis-cyanopropyl</i>	80% <i>bis-cyanopropyl</i>	<i>OV-275</i> **	85% <i>bis-cyanopropyl</i> ***
10% <i>diphenyl</i>	15% <i>dimethyl</i>		13% <i>p-tolyl</i>
5% <i>vinyl</i>	5% <i>vinyl</i>		2% <i>XX-4</i>
1 C ₁₅	1 C ₁₅	1 C ₁₅	1 C ₁₅
2 C ₁₇	2 C ₁₇	2 C ₁₇	2 Octanol
3 Octanol	3 Octanol	3 Octanol	3 Cyclooctane
4 Cyclooctanone	4 C ₁₈	4 C ₁₈	4 C ₁₇
5 C ₁₈	5 C ₁₉	5 C ₁₉	5 C ₁₈
6 C ₁₉	6 Cyclooctanone	6 Cyclooctanone	6 Naphthalene
7 Naphthalene	7 Naphthalene	7 Naphthalene	7 C ₁₉
8 2,6-Dimethylphenol	8 2,6-Dimethylphenol	8 2,4-Dimethylaniline	8 2,6-Dimethylphenol
9 2,4-Dimethylaniline	9 2,4-Dimethylaniline	9 2,6-Dimethylphenol	9 2,4-Dimethylaniline

TABLE I (continued)

(E) SP 2340**	(F) 95% Cyanopropyl-methyl 5% vinyl	(G)	(H) 85% Cyanopropyl-methyl 10% diphenyl 5% vinyl
1 C ₁₅	1 C ₁₅	1 C ₁₅	1 C ₁₅
2 C ₁₇	2 Octanol	2 Octanol	2 Octanol
3 C ₁₈	3 Cyclooctanone	3 Cyclooctanone	3 Cyclooctanone
4 Octanol	4 C ₁₇	4 C ₁₇	4 C ₁₇
5 Cyclooctanone	5 Naphthalene	5 Naphthalene	5 Naphthalene
6 C ₁₉	6 C ₁₈	6 2,6-Dimethylphenol	6 C ₁₈
7 Naphthalene	7 C ₁₉	7 C ₁₈	7 2,6-Dimethylphenol
8 2,6-Dimethylphenol	8 2,6-Dimethylphenol	8 2,4-Dimethylaniline	8 2,4-Dimethylaniline
9 2,4-Dimethylaniline	9 2,4-Dimethylaniline	9 C ₁₉	9 C ₁₉
(I) 48% bis-cyanopropyl*** 16% <i>p</i> -tolyl 36% dimethyl	(J) 75% Cyanopropyl-methyl 20% dimethyl 5% vinyl	(K) 75% Cyanopropyl-methyl 20% diphenyl 5% vinyl	(L) 30% Cyanopropyl-methyl 65% dimethyl 5% vinyl
1 C ₁₅	1 Octanol	1 Octanol	1 Octanol
2 Octanol	2 C ₁₅	2 C ₁₅	2 Cyclooctanone
3 Cyclooctanone	3 Cyclooctanone	3 Cyclooctanone	3 2,6-Dimethylphenol
4 C ₁₇	4 Naphthalene	4 Naphthalene	4 Naphthalene
5 Naphthalene	5 C ₁₇	5 C ₁₇	5 2,4-Dimethylaniline
6 C ₁₈	6 2,6-Dimethylphenol	6 2,6-Dimethylphenol	6 C ₁₅
7 2,6-Dimethylphenol	7 2,4-Dimethylaniline	7 C ₁₈	7 C ₁₇
8 2,4-Dimethylaniline	8 C ₁₈	8 2,4-Dimethylaniline	8 C ₁₈
9 C ₁₉	9 C ₁₉	9 C ₁₉	9 C ₁₉
(M) 15% Cyanopropyl 80% dimethyl 5% vinyl			
1 Octanol			
2 Cyclooctanone			
3 2,6-Dimethylphenol			
4 Naphthalene			
5 2,4-Dimethylaniline			
6 C ₁₅			
7 C ₁₇			
8 C ₁₈			
9 C ₁₉			

* High-molecular-weight high-viscosity phases on a 25 m × 0.25 mm I.D. fused-silica capillary column.

** Commercial phases on hydrogen chloride-treated 25 m × 0.25 mm I.D. soft glass capillary columns.

*** Provided by Professor Milton L. Lee, Brigham Young University, Provo, UT, U.S.A.

low molecular weights and viscosity of these commercial materials, they could not be applied successfully to the untreated fused-silica glass surface¹. The precise chemical nature of these substances is generally not available.

For reasons not readily apparent at this time, the polymer containing 85% bis-cyanopropyl, 13% *p*-tolyl (Fig. 4, Table I, D) does not exhibit the same degree of polarity as others with the same moiety.

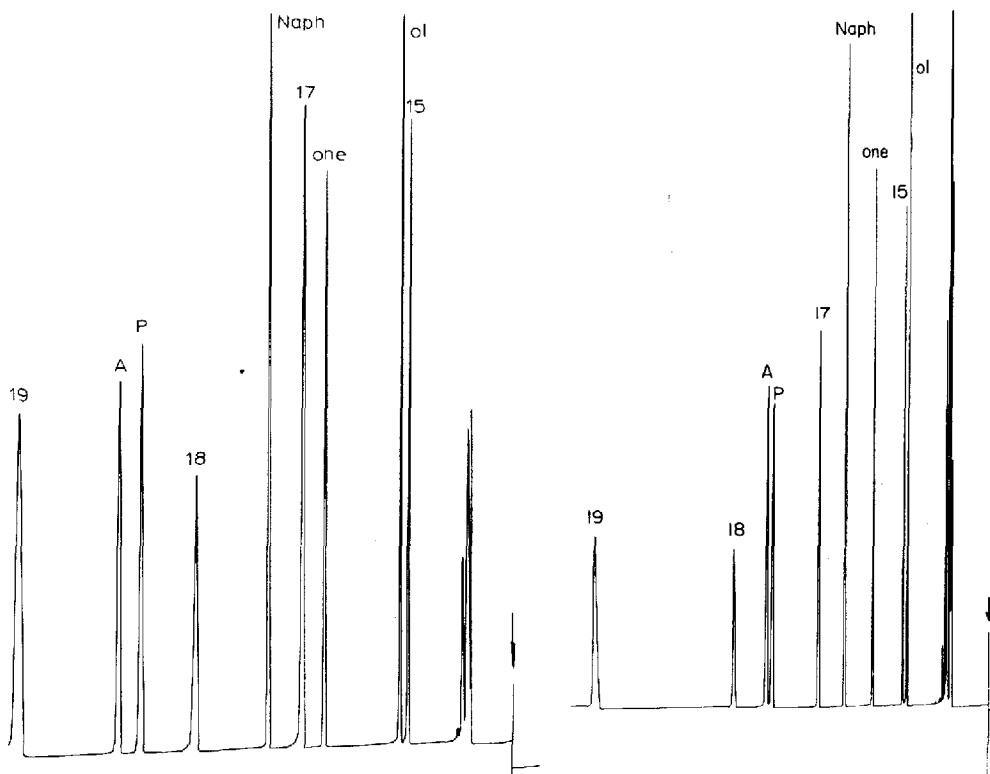


Fig. 7. Analysis of a polar test mixture on a fused-silica capillary column (25 m \times 0.25 mm) containing a cyanosilicone polymer (48% bis-cyanopropyl, 16% *p*-tolyl, 36% dimethyl) coated onto the untreated glass surface. The tailing of the hydrocarbons is due to selective adsorption by this particular phase. Temperature, 110°C; pressure, 15 p.s.i. hydrogen; chart speed 60 cm/h. Peaks as in Fig. 3.

Fig. 8. Analysis of a polar test mixture on a fused-silica capillary column containing a cyanosilicone polymer (75% cyanopropyl methyl, 20% dimethyl, 5% vinyl) coated onto the untreated glass surface. Column dimensions and conditions as in Fig. 7, except pressure: 16 p.s.i. hydrogen. Peaks as in Fig. 3.

The presence of cyanopropyl methyl substitutions (Table I, F, H, J and K, Figs. 5, 6, 8 and 9) also imparts "polarity" to the polymers but the effect is not as pronounced as that noted with bis-cyanopropyl functionality. When either the bis-cyanopropyl or the cyanopropyl methyl content dropped below 50% (Table I, L and M, Fig. 10) the hydrocarbons are decidedly retarded and emerge last from the column. Diphenyl groups (Table I, A, H and K, Figs. 6 and 9) associated with either substituent seemed to impart only a slight degree of selectivity in the order of emergence of certain of the components from the column.

It is of interest to note that in the analysis of the methyl esters of straight chain saturated and unsaturated fatty acids on columns coated with polymers having a high bis-cyanopropyl content¹², the C-20:0 saturated methyl ester was eluted before the C-18:3 component band (Figs. 11 and 12). With other types of cyanopropyl substitution, the C-20:0 emerged after the C-18:3.

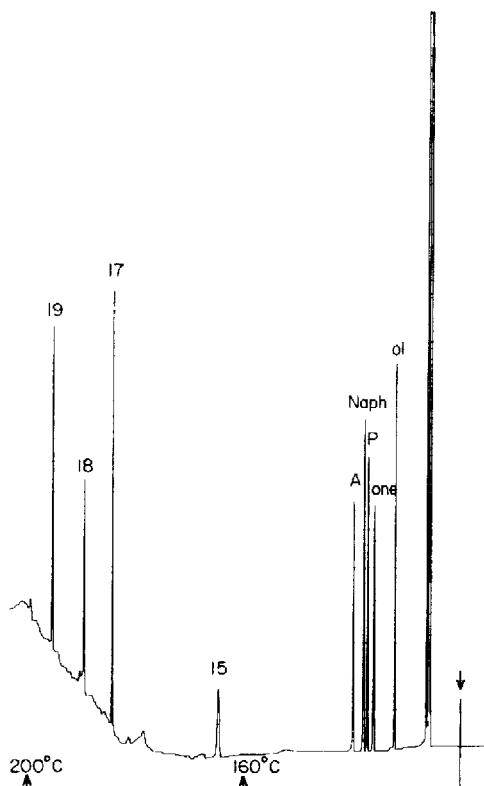


Fig. 9. Analysis of a polar test mixture on a fused-silica capillary column containing a cyanosilicone polymer (75% cyanopropyl methyl, 20% diphenyl, 5% vinyl) coated onto the untreated glass surface. Note slight "tail" on alcohol (ol) peak and depressed dimethyl aniline (A) peak denoting slight activity of column surface. Column dimensions and conditions as in Fig. 3, except pressure: 13 p.s.i. hydrogen. Number of plates per meter for C_{19} : 4050. Peaks as in Fig. 3.

Deactivation and wetting by polar phases

The high-molecular-weight, high-viscosity polar polymers described in this study for the most part provided excellent deactivation and wetting of the *untreated* fused-silica surfaces. If the polymers were purified by repeated precipitation by methanol followed by exhaustive solvent washing and no traces of the catalyst used in the polymerization remained, excellent peak shapes were almost universally noted. Under these circumstances, homogeneous film formation was encountered and column efficiencies ranged from 3000 to over 4000 plates/m. Those phases containing appreciable bis-cyanopropyl substitution were particularly susceptible to oxidation¹⁹ and oxygen scrubbers had to be employed routinely. Although an occasional polar polymeric film showed bead formation upon temperature cycling, most polymers were stable to 220–250°C.

Cross-linking and solvent extraction (immobilization)

The results obtained after adequate exposure to the free radical generator

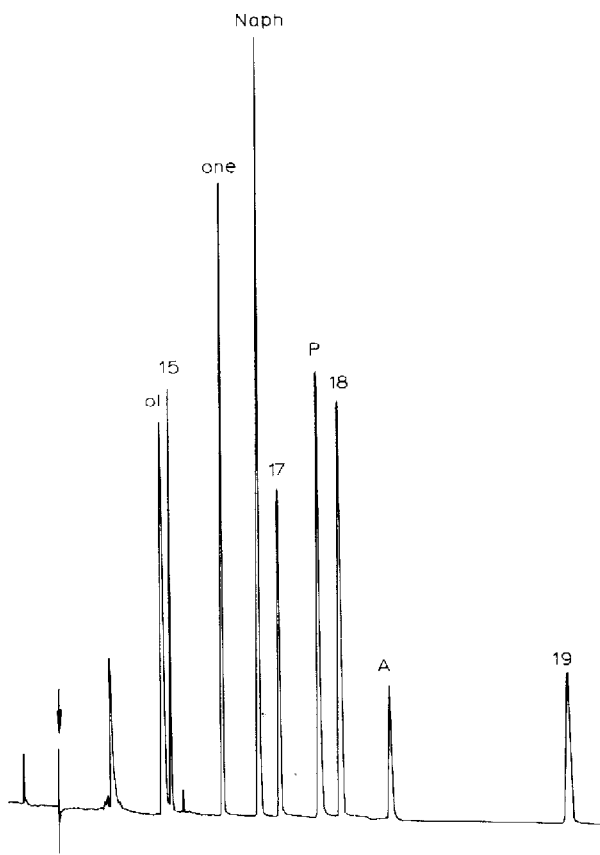


Fig. 10. Analysis of a polar test mixture on a fused-silica capillary column (25 m \times 0.25 mm) containing a cyanosilicone polymer (15% cyanopropyl, 80% dimethyl, 5% vinyl) coated onto the untreated glass surface. Note the slight "tail" on the alcohol (ol) and dimethyl aniline (A). This essentially is a non-polar column. The hydrocarbons were severely retarded. Temperature, programmed from 120 to 200°C; pressure, 14 p.s.i. hydrogen; chart speed, 60 cm/h. Peaks as in Fig. 3.

azo-*tert.*-butane were varied despite the presence of adequate vinyl or tolyl groups. Columns coated with the very polar polymers (high bis-cyanopropyl content) showed very little evidence of vulcanization. Only residual amounts of phase remained (trace to *ca.* 20%) after solvent washing. Markides *et al.*¹² and Richter *et al.*¹⁸ also encountered certain of these difficulties with some of their cyanosilicone phases. On the other hand, in those instances where the stationary phase polymers had no more than 75% cyanopropyl methyl substitution and no diphenyl moieties (Table I, J and Fig. 8) extensive cross-linking readily occurred and upon solvent rinsing only 15–20% of the phase did not appear to be immobilized. Compared with that noted with non-polar phases this figure is somewhat high. Depending upon precise structural characteristics, it appears that the cyanopropyl moiety can sterically hinder the vulcanization reaction to a considerable degree even in the presence of vinyl or tolyl groups.

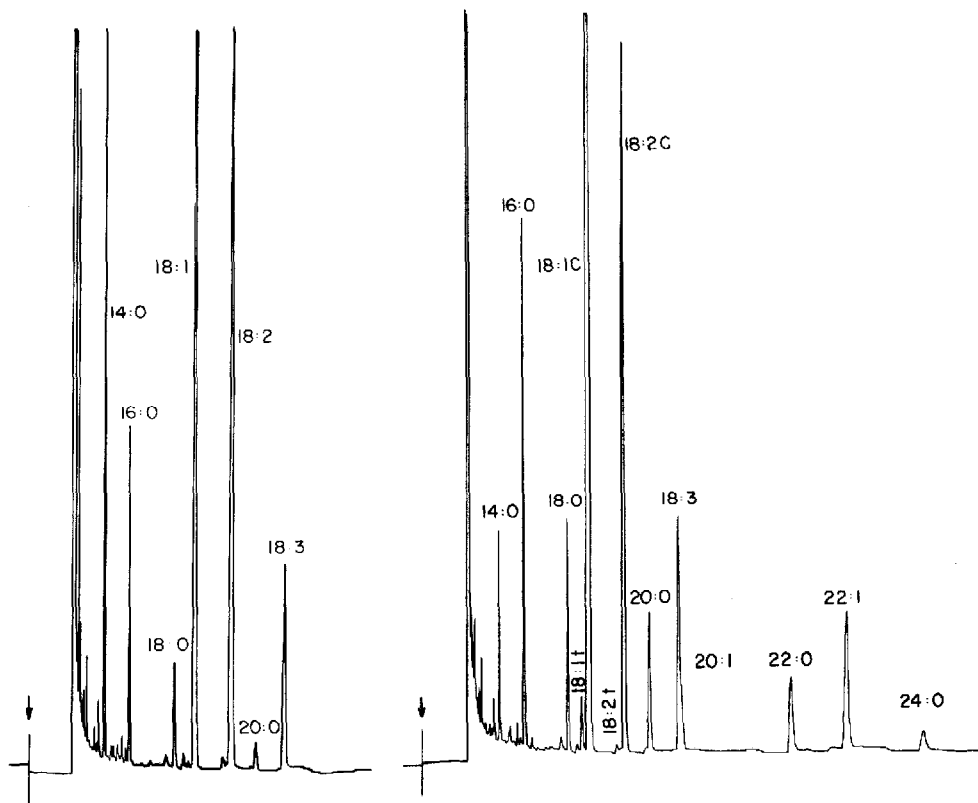


Fig. 11. Analysis of a sample of saturated and unsaturated straight chain methyl ester of fatty acids on a fused-silica capillary column (25 m \times 0.25 mm) containing a cyanosilicone polymer (85% bis-cyanopropyl, 10% phenyl, 5% methyl vinyl). Note C-20:0 emerging before C-18:3. Temperature, 170°C; pressure, 14 p.s.i. hydrogen; chart speed, 60 cm/h.

Fig. 12. Analysis of a sample of the methyl esters of fatty acids of rapeseed oil. Column and conditions as in Fig. 11.

Covalently bonding of polar phases to untreated fused-silica surface

On the basis of some of the data presented here, there is no reason whatsoever to believe that these polar stationary phases chemically react with silanol groups on the untreated fused-silica to covalently bond² the polymer to the surface of the glass wall. Further, also based on these preliminary findings at this time, it does not appear that this type of reaction is mandatory for the successful deactivation, wetting, cross-linking and immobilization of polar stationary phases on fused-silica glass. In this regard, we have attempted to increase the cross-linking reaction with certain suitable polar polymers towards 100% by "precoating" a thin layer of these polymers onto the untreated fused-silica surface prior to recoating with the same or in some instances chemically similar polymers to obtain a fully cured column with an average film thickness of *ca.* 0.25 μ m. Inevitably, "beading" and all its dire consequences occurred. In this regard, it is interesting to note that Markides *et al.*¹² precoated hydrochloric acid-treated fused-silica columns with cyclic cyanosiloxanes or other cyanosilicones

prior to the regular application of the polar cyanopropyl phase. However, even under these circumstances, there was no evidence to indicate that cross-linking occurred to a degree greater than that reported here.

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REFERENCES

- 1 S. R. Lipsky and W. J. McMurray, *J. Chromatogr.*, 279 (1983) 59.
- 2 K. Grob and G. Grob, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 3 (1983) 153-155.
- 3 S. R. Lipsky and W. J. McMurray, *J. Chromatogr.*, 239 (1982) 61-69.
- 4 B. W. Wright, P. A. Peaden, M. L. Lee and T. Stark, *J. Chromatogr.*, 248 (1982) 17.
- 5 T. Juutilainen and J. Enqvist, *J. Chromatogr.*, 279 (1983) 91.
- 6 M. Verzele, F. David, M. van Roelenbosch, G. Diricks and P. Sandra, *J. Chromatogr.*, 279 (1983) 99.
- 7 W. Patnode and D. F. Wilcock, *J. Amer. Chem. Soc.*, 68 (1946) 358.
- 8 C. Madani, E. M. Chambaz, M. Rigaud, J. Durand and P. Chebroux, *J. Chromatogr.*, 126 (1976) 161-169.
- 9 C. Madani and E. M. Chambaz, *J. Amer. Oil Chem. Soc.*, 58 (1981) 63-69.
- 10 J. Buijten, L. Blomberg, K. Markides and T. Wännman, *J. Chromatogr.*, 237 (1982) 465-468.
- 11 P. A. Peaden, B. W. Wright and M. L. Lee, *Chromatographia*, 15 (1982) 335-340.
- 12 K. Markides, L. Blomberg, J. Buijten and T. Wännman, in J. Rijks (Editor), *Proceedings of the Fifth International Symposium on Capillary Chromatography*, Elsevier, Amsterdam, 1983, pp. 117-126.
- 13 B. W. Wright, P. A. Peaden and M. L. Lee, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 5 (1982) 413-416.
- 14 J. J. Kirkland and J. J. DeStefano, *J. Chromatogr. Sci.*, 8 (1970) 309.
- 15 C. R. Hastings, J. M. Augl, S. Kapila and W. A. Aue, *J. Chromatogr.*, 87 (1973) 49.
- 16 R. E. Majors and M. J. Hopper, *J. Chromatogr. Sci.*, 12 (1974) 767.
- 17 S. R. Lipsky, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1983) 359-365.
- 18 B. E. Richter, J. C. Kuei, J. I. Shelton, L. W. Castle, J. S. Bradshaw and M. L. Lee, *J. Chromatogr.*, 279 (1983) 21.