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POLARIZABLE POLYSILOXANE STATIONARY PHASES FOR CAPILLARY COLUMN GAS CHROMATOGRAPHY

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SUMMARY

Polysiloxane polymers, containing polarizable biphenyl, naphthyl and phenoxyphenyl side groups, were synthesized and evaluated for capillary column gas chromatography. Although the more polar cyanopropyl stationary phase demonstrated better resolution of components in a wide-polarity-range mixture, the polarizable phases demonstrated better resolution of polar isomers. The "softer" dipole–induced dipole interaction between the solute and stationary phase, as compared to the dipole–dipole interaction with a polar stationary phase, is more sensitive to slight molecular differences in isomeric structures. The biphenyl polysiloxane, on the whole, demonstrated the best selectivity in a number of isomer separations.

INTRODUCTION

The two factors affecting resolution in all forms of chromatography are efficiency and selectivity. In gas chromatography (GC), the mobile phase participates only as a carrier, and exhibits little, if any, effect on selectivity. Thus, the stationary phase is primarily responsible for the chromatographic separation obtained. Factors such as stationary phase viscosity, composition, structure, *e.g.*, highly cross-linked, thermal stability and film uniformity are all important. These considerations have led to recent efforts to design and tailor-make stationary phases possessing the highest performance characteristics.

The main advantage of using capillary columns in GC is their high efficiency. For the separation of components in complex mixtures, selectivity becomes much less important. While the resolution of many components can be improved by changing their relative migration rates (retention), the resolution of other components can be simultaneously decreased[1].

This reasoning is now widely understood and accepted. Ever increasing numbers of analysts are turning from packed columns to capillary columns to solve their resolution problems. Since the high viscosity methylpolysiloxanes have historically provided the highest efficiencies[2], they are presently the most widely used stationary phases in capillary column GC. However, newly applied cross-linking technology for stationary phase immobilization has allowed higher efficiencies and thermal stabilities

for the more polar phases. It seems reasonable to expect that capillary columns exhibiting high efficiencies and selectivities different from the methylpolysiloxanes should soon become common for many applications in which peak identification must be confirmed by chromatography on a column of different polarity, and where critical solute pairs cannot be properly resolved on an apolar column.

Stationary phase selectivity is derived from the interactions between the solute and stationary phase. These can include charge transfer, hydrogen bonding, acid–base, dipole–dipole, dipole–induced dipole and dispersion forces. The dispersion forces are the most difficult to describe, but are related to the non-polar intermolecular forces (induced dipoles) that lead to the common observation that "like dissolves like". Unfortunately, solute–stationary phase interactions are usually a combination of these forces, making very difficult the selection of a stationary phase based on specific interactions.

Early efforts to characterize stationary phases according to polarity were generally based on the retention of a polar solute on columns containing the different phases. For instance, Rohrschneider[3] suggested that the retention index of benzene, measured at a given temperature, was a precisely measurable quantity of general importance for stationary phase characterization, and that it gave a more or less valid indication of GC polarity. However, this "overall" polarity measurement by means of a single quantity was inadequate for describing the intermolecular interactions between solute and stationary phase.

Rohrschneider[3–5] was the first to classify stationary phases according to solute–stationary phase interactions. He used the retention times of benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine to calculate polarity constants. McReynolds[6] expanded this system by substituting butanol for ethanol, 2-pentanone for methyl ethyl ketone and nitropropane for nitromethane as well as by adding five additional compounds. The solute–stationary phase interactions were classified as dispersion (benzene), electron attraction (butanol), electron repulsion (2-pentanone) and two undefined types (nitropropane and pyridine). It was suggested that one of these interaction types would dominate for any solute. Thus, electron attraction would dominate for alcohols, while electron repulsion would dominate for ethers or ketones.

McCloskey and Hawkes[7] have further analyzed McReynolds' data by using a two-dimensional plot of polarity *versus* dispersion. This analysis, as it relates to capillary GC, was also discussed by Stark *et al.*[8]. A comprehensive evaluation of polarity factors was also reported by Semenchenko and Vigdergauz[9]. Based on results from these analyses, "preferred" stationary phases have been proposed[8–10].

While the extensive polarity classification studies mentioned above have been valuable in determining suitable stationary phases for specific applications, there still remain serious shortcomings in these approaches. This is a result of the complexities involved in molecular interactions. For instance, the phenyl-containing methylpolysiloxanes are non-polar and were generally believed to exhibit only dispersion forces. Recently, Brady *et al.*[11] have conducted a solvatochromic investigation of a series of phenyl-containing polymers and have found a low level of hydrogen-bonding acceptor character in addition to larger polarizability effects. In another example, an alcohol can have hydrogen bonding (both acceptor and donor), dipole–dipole, dipole–induced dipole and dispersion interactions, depending on the stationary

phase. Rohrschneider[3] suggested that solute molecular size could also affect solute-stationary phase interactions.

The foregoing discussion is not meant to be a comprehensive review of the classification of stationary phases, but rather a summary of the developments in this area. It is obvious that the problem is complex, and the solutions are far from satisfactory. Based on the resultant classifications, columns can be more effectively selected for the separation of mixture components of differing polarities, but these schemes are of little help in solving the main resolution problems encountered in capillary column GC —the separation of isomers or other compounds with very similar properties.

Recently, a newly synthesized biphenyl polysiloxane stationary phase was reported[12]. This polarizable polymer exhibited predominantly dispersion and dipole–induced dipole interactions, and has demonstrated superior resolution of the amino-phenanthrene isomers when compared to the more polar cyanopropyl polysiloxane phase. The "softer" dipole–induced dipole interaction between the polar solute and polarizable stationary phase was more sensitive and, therefore, more selective for minor differences in molecular structure than the dipole–dipole interaction between the polar solute and polar cyanopropyl stationary phase.

In this study, two new polarizable stationary phases, containing naphthyl and phenoxyphenyl functional groups, were synthesized. The characteristics and performance of these phases compared to the biphenyl phase as well as to the conventional non-polar (methyl and phenyl) and polar (cyanopropyl) phases were investigated.

EXPERIMENTAL

Synthesis of polysiloxane stationary phases

Biphenyl phases. The synthesis of a 25% biphenyl polysiloxane phase was reported previously[12]. A 36% biphenyl, 14% n-octyl polysiloxane was prepared by hydrolyzing 2.33 g of biphenylmethyldimethoxysilane[12] and 0.22 g of n-octylme-thyldimethoxysilane[13] in 30 ml of acetonitrile and deionized water (1:1) for 10 h. The solvent was decanted and the hydrolyzed monomers were heated at 130°C for 1 h to remove excess of solvent. A small amount of 10% KOH in methanol (equal to 0.05% of the polymer) was added and the mixture was heated at 130°C for 5 h in a nitrogen stream. The polymer was end-capped at room temperature with a 1:2 mixture of 1,3-divinyltetramethyldisilazane and vinyldimethylchlorosilane in 10 ml of methylene chloride. The resulting polymer was precipitated by adding 10 ml of methanol to the methylene chloride solution. The polymer was dissolved in 10 ml of methylene chloride and again precipitated with methanol. The fractionation process was repeated eight times before the polymer was dried overnight under vacuum.

1-Naphthyl phase. The 33% 1-naphthyl polysiloxane phase was prepared after first synthesizing 1-naphthylmethyldimethoxysilane, as reported for the biphenyl analog, by a Grignard reaction[12]. The phase was synthesized by first allowing equimolar amounts (8.3 mmole) of 1-naphthylmethyldimethoxysilane and dimethyldimethoxy-silane to react overnight in 20 ml of water–acetonitrile (1:1). The hydrolyzed monomers were then extracted with methylene chloride and the water–acetonitrile mixture was discarded. One drop of a 10% (w/w) solution of tetramethylammonium hy-droxide in methanol was added to the extract. The monomers were then heated from

40 to 115°C at 0.5°C min⁻¹. The final temperature was held for 1.75 h, and the polymer was dissolved in methylene chloride and end-capped over a 12-h period with a 1:2 mixture of 1,3-divinyltetramethyldisilazane and vinyldimethylchlorosilane. The methylene chloride solution was washed three times with an equal volume of water, followed by precipitation of the polymer with methanol. The polymer was then dissolved in methylene chloride and precipitated with methanol six more times. The polymer was dried overnight in a vacuum oven to give 650 mg of finished polymer. NMR analysis of this polymer showed that it was composed of 33% naphthalene units.

    Phenoxyphenyl phase. 4-Phenoxyphenylmethyldimethoxysilane monomer was prepared as follows. *p*-Bromodiphenyl ether (62.0 ml, 0.4 mole) in 500 ml of anhydrous diethyl ether was slowly added to 10.21 g (0.420 mole) of magnesium in 40 ml of anhydrous ether under nitrogen. The solution was refluxed for 5 h and allowed to cool. It was then added under nitrogen over a period of 20 min to 60.0 ml (0.420 mole) of methyltrimethoxysilane (Petrarch, Bristol, PA, U.S.A.) in 200 ml of anhydrous ether. The reaction mixture was then refluxed overnight, cooled and filtered through Celite. The solid residue was washed with two 100-ml portions of ether and the combined ether filtrate and washings were concentrated under vacuum. The solid residue was dissolved in hexane and filtered. The solvent was removed under vacuum, and the residue was distilled to give 4-phenoxyphenylmethyldimethoxysilane as a colorless oil, b.p. 126–134°C/0.8 mmHg, 51.77 g (47%). IR (cm⁻¹): 2940, 2840, 1580, 1490, 1240, 1080, 830, 800. NMR (δ): 7.57–6.90 (9H, mult.), 3.54 (6H,s), 0.34 (3H,s).

    The 50% 4-phenoxyphenyl polysiloxane gum was prepared by allowing 2.01 g (7.33 mmole) of 4-phenoxyphenylmethyldimethoxysilane to react with 19.1 mg (144 μmole) of vinylmethyldimethoxysilane and 9.5 mg of 1,4-dimethyl-1,1,4,4-tetramethoxydisilethylene in 12 ml of acetonitrile–water (1:1). After stirring the mixture overnight, four drops of 10% (w/w) tetramethylammonium hydroxide in methanol were added and it was placed in an oven under a continuous stream of nitrogen. The temperature was programmed from 40 to 115°C at 0.5°C min⁻¹. An additional four drops of tetramethylammonium hydroxide solution were added after 8 h. Heating was continued for a total of 24 h. The residue was dissolved in methylene chloride and end-capped overnight at room temperature with two drops of vinyldimethylchlorosilane and six drops of divinyltetramethyldisilazane. The reaction mixture was washed with three *ca.* 4-ml portions of water and filtered. The polymer phase was precipitated from the methylene chloride solution with methanol. The residue was dissolved in methylene chloride and precipitated with methanol seven more times and dried in vacuum at 57°C to give a clear, colorless gum (414.6 mg).

Capillary column preparation

    Fused-silica capillary columns (10 m × 0.31 mm I.D.; Hewlett-Packard, Avondale, PA, U.S.A.) were statically coated with 1-μm film thicknesses of SE-54, OV-1 (both from Applied Science Labs., State College, PA, U.S.A.), Superox 20M (gift from M. Verzele, Ghent, Belgium), 50% phenyl polysiloxane[14], 25% biphenyl polysiloxane[12], 36% biphenyl polysiloxane, 33% naphthyl polysiloxane, 50% phenoxyphenyl polysiloxane, 50% cyanopropyl polysiloxane[15] and 88% cyanopropyl polysiloxane[16] (all synthesized in this laboratory). All phases were coated in solutions of methylene chloride, except for SE-54 and OV-1, which were dissolved in *n*-pentane.

Cross-linking was accomplished by purging each column with azo-*tert.*-butane vapors in nitrogen gas at room temperature for 1 h (flow-rate 3 ml min^{-1}), sealing both ends of the column with a micro-torch, heating the column from 40 to 220°C at 4°C min^{-1} and holding the upper temperature for 1 h. Cross-linking was not attempted for the Superox 20M columns. All columns except the Superox 20M columns were conditioned by programming from 40 to 230°C at 1°C min^{-1} and holding at 230°C for 10 h, using a nitrogen gas flow. The Superox 20 M column was conditioned at 130°C for 30 min under a helium gas flow.

Five additional 20 m × 0.31 mm I.D. fused-silica columns were coated with 0.25-μm films of SE-54, 25% biphenyl polysiloxane, 50% phenoxyphenyl polysiloxane, 50% phenyl polysiloxane and 88% cyanopropyl polysiloxane. The cross-linking and conditioning procedures were as previously described, except that the upper temperature for conditioning was 280°C.

Gas chromatography

The capillary columns containing 1-μm stationary phase film thicknesses were tested for polarity in an HP 5790 gas chromatograph equipped with a splitless injector and flame ionization detector. The hydrogen carrier-gas linear velocity was approximately 68 cm sec^{-1}, and the chromatographic oven was maintained at 125°C for the analyses. Standard solutions of biphenyl and *n*-alkanes in methylene chloride were injected into the gas chromatograph for determination of the retention indices of biphenyl. In most cases, three columns were evaluated for each stationary phase.

Several standard compound mixtures and selected fractions of a coal liquid were chromatographed on the 20-m columns coated with 0.25-μm stationary phase films. The hydrogen carrier-gas velocity was set at approximately 100 cm sec^{-1}, and the oven was programmed at 4°C min^{-1}. For these analyses, an HP 5880 gas chromatograph equipped with a splitless injector and both flame ionization and sulfur-selective flame photometric detectors was used.

Thermal gravimetric analysis

A Perkin-Elmer DSC-2 differential scanning calorimeter was used to analyze several of the polymer phases. The temperature was programmed from 100 to 500°C at 10°C min^{-1} for each analysis. Measurements were made in both nitrogen and air atmospheres.

RESULTS AND DISCUSSION

Biphenyl can be used as a test compound to measure the general polarity of stationary phases in capillary GC. As mentioned in the Introduction, benzene has been used for this purpose for packed columns, but its low retention in capillary columns makes the measurement difficult. Biphenyl is also more polarizable, and should be more sensitive to stationary-phase polarity changes. Table I lists the retention indices (RI) of biphenyl for the polarizable stationary phases reported here, along with several conventional non-polar and polar stationary phases. The RIs for the polarizable phases all lie within 125 index units, with the 25% biphenyl phase exhibiting the lowest polarity and the 50% phenoxyphenyl phase exhibiting the highest polarity. Fig. 1 shows the structures of these polarizable phases. The biphenyl

TABLE I

RETENTION INDICES OF BIPHENYL ON SELECTED STATIONARY PHASES

Stationary phase	RI*	S.D.
100% Methyl polysiloxane (OV-1)	1353.4	0.5
5% Phenyl, 1% vinyl, 94% methyl polysiloxane (SE-54)	1385.1	1.2
25% Biphenyl, 1% vinyl, 74% methyl polysiloxane	1563.8	6.1
33% Naphthyl, 67% methyl polysiloxane	1594.5***	—
36% Biphenyl, 14% *n*-octyl, 50% methyl polysiloxane	1605.4	2.4
50% Phenyl, 1% vinyl, 49% methyl polysiloxane	1619.9	1.3
50% Phenoxyphenyl, 2% vinyl, 48% methyl polysiloxane	1686.8	1.1
Polyethylene glycol (Superox 20M)	1964.0**	2.3
50% Cyanopropyl, 10% *p*-tolyl, 40% methyl polysiloxane	2001.1**	11.3
88% Cyanopropyl, 10% *p*-tolyl, 2% methyl polysiloxane	2241.6	11.6

    * Average of measurements on three columns.
   ** Average of measurements on two columns.
 *** Measurement on one column.

phase has the lowest concentration of polarizable functional groups and the highest concentration of methyls. The phenoxyphenyl group has some polar character because of the ether oxygen between the two aromatic rings. As a group, the polarizable phases demonstrate greater polarity than OV-1 and SE-54. This is a result of the dispersion forces exerted by the aromatic rings.

    The measurement of stationary phase polarity by using a polarizable solute
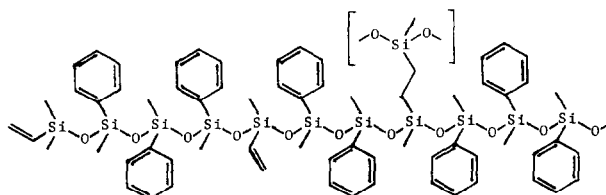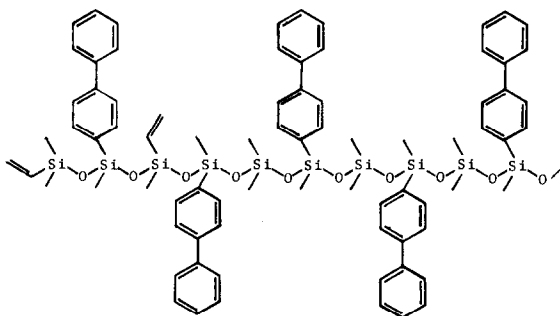

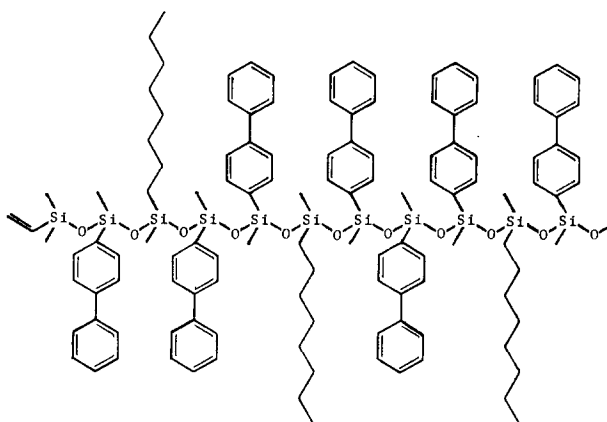50% phenyl, 1% vinyl methylpolysiloxane
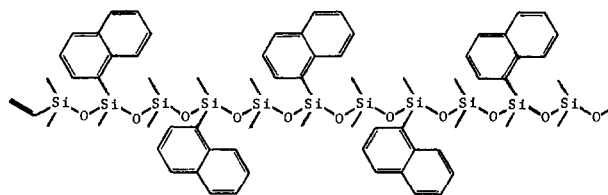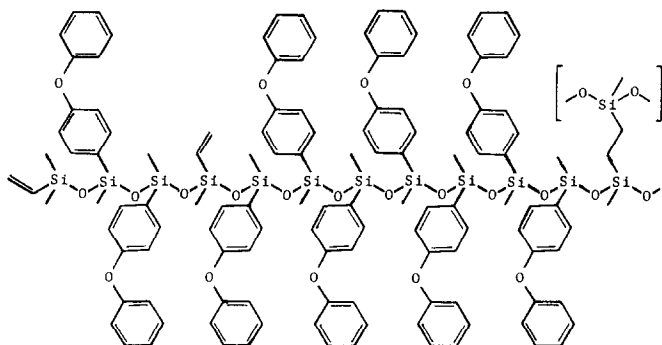

33% naphthyl methylpolysiloxane

Fig. 1.

25% biphenyl, 1% vinyl methylpolysiloxane

36% biphenyl, 14% n-octyl methylpolysiloxane

50% phenoxyphenyl, 2% vinyl methylpolysiloxane

Fig. 1. Chemical structures of the polarizable polysiloxane stationary phases.

TABLE II

AVERAGE MOLECULAR POLARIZABILITIES OF AROMATIC MOLECULES

Compound	Structure	Average molecular polarizability (δ)
Benzene		10.4*
Naphthalene		16.6*
Biphenyl		20.0**
Diphenyl ether		21.7**

* Taken from ref. 17.
** Calculated by the method described in ref. 17.

such as biphenyl is more valid than the use of polar solutes. When biphenyl is used, the only significant interactions that are present between the stationary phase and solute are dipole–induced dipole and dispersion. The extent to which the biphenyl molecule is polarized by the stationary phase determines its retention on the chromatographic column, and indicates the polarity of the stationary phase. A comparison of the retention indices of biphenyl on different stationary phases provides a more realistic picture of the relative polarities of these phases than does the common practice of summing the McReynolds polarity constants. The latter method yields extremely high values for the more polar phases, giving the false impression that these phases are much more polar than the moderately polar ones.

Table II lists the average molecular polarizabilities of the functional groups that were incorporated into the polarizable stationary phases in this study. The biphenyl and phenoxyphenyl groups were the most polarizable, and demonstrated the best chromatographic selectivity for a number of applications. Since the net polarizability of any phase could be increased by increasing the content of polarizable functional groups in the polymer, attempts were made to maximize this content. In a previous study[12] it was found that increasing the biphenyl content above 25% in a biphenylmethyl polysiloxane polymer resulted in a solid instead of a gum product, It was found in this study that with 14% *n*-octyl groups in the polymer the biphenyl content could be increased to 36%. The *n*-octyl groups also facilitated cross-linking, but decreased the thermal stability of the stationary phase. The synthetic procedure for the biphenyl-*n*-octyl polymer was designed to give 45% biphenyl and 5% *n*-octyl, but the analysis of the polymer by ¹H NMR spectroscopy verified a lower biphenyl and higher *n*-octyl content. The lower-molecular-weight fraction of the polymer that was eliminated during fractional precipitation probably had a higher biphenyl content. Similarly, equimolar amounts of 1-naphthylmethyldimethoxysilane and dimethyldimethoxysilane were mixed to yield a 25% naphthyl polymer. However, ¹H NMR analysis indicated 33% naphthyl.

A small amount of 1,4-dimethyl-1,1,4,4-tetramethoxydisilethylene was added to the phenoxyphenyl polymer in order to increase the polymer viscosity. This was found to be important in the synthesis of the phenyl-containing polymers previously obtained in this laboratory[14].

Unlike stationary phases that are designed for specific solute–stationary phase interactions and, therefore, are only applicable to certain separations, the polarizable

stationary phases are more universally applicable. The phenyl, biphenyl, phenoxy-phenyl and naphthyl functional groups are essentially non-polar, and phases incor-porating these groups can be used as apolar phases. These non-polar functional groups, however, contain mobile π-bonding electrons and may acquire dipole mo-ments when exposed to an electric field or to polar compounds. This induced dipole is a result of distortion of their electron distributions, forming centers of positive and negative charge. The magnitude of the induced dipole is proportional to the energy of the highest occupied molecular orbital (HOMO). Biphenyl, with ten π-bonding electrons in two rings, has a HOMO of higher energy and, hence, has a higher po-larizability than benzene which has six π-bonding electrons in one ring. Stationary phases containing polarizable groups offer selectivity for any type (electron acceptor or electron donor) of polar solute.

Fig. 2 compares the retention times of components in a wide-polarity mixture on five different stationary phases under standardized conditions. Dispersion inter-actions are responsible for the greater retention of n-eicosane on the non-polar and polarizable phases, and for the greater retention of biphenyl and 4-phenylpyridine on the polarizable phases. Dipole–induced dipole interactions are responsible for the even greater retention of 4-hydroxybiphenyl and 4-aminobiphenyl on the polarizable phases. Dipole–dipole interactions lead to the greatest retention of these compounds
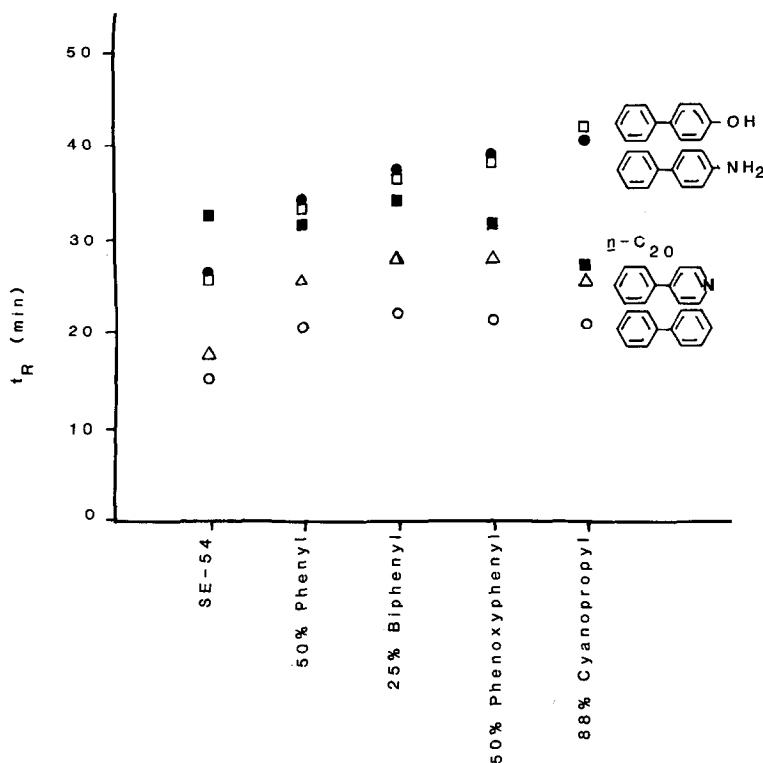

Fig. 2. Retention times, t_R, of standard compounds in a wide-polarity mixture on five different stationary phases. For chromatographic conditions see text.
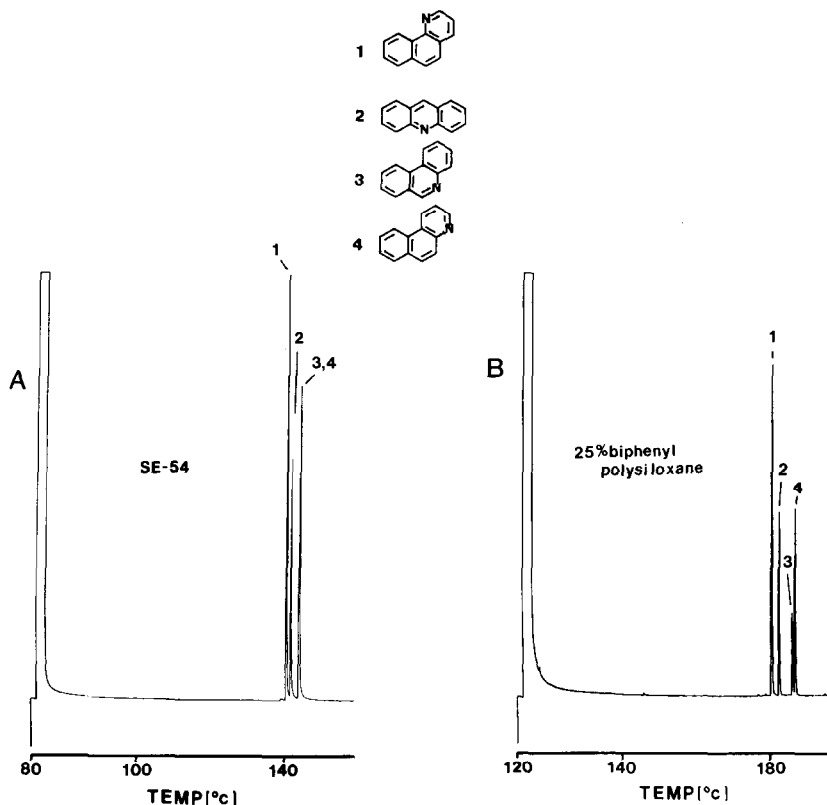
Fig. 3. Chromatograms of isomeric nitrogen heterocycles on SE-54 (A) and 25% biphenyl polysiloxane (B) stationary phases. For conditions see text.

on the polar cyanopropyl polysiloxane stationary phase. The greatest spread in retention for the components in this mixture was obtained on the cyanopropyl phase. This indicates that the best separation of components of somewhat differing polarities ought to be obtained on a polar stationary phase. Figs. 3 and 4 show chromatograms of four isomeric nitrogen heterocycles on several different stationary phases. The polarity of each compound is determined by the position of the nitrogen atom in the aromatic structure. As expected, the polar cyanopropyl stationary phase provides the best resolution of these compounds, although the biphenyl phase demonstrates nearly the same performance.

Isomers with more subtle differences in their structures are usually more difficult to resolve. Figs. 5 and 6 show chromatograms of the four methylcarbazoles. In this case, the strong dipole–dipole interactions between the solutes and the cyanopropyl functional groups result in significantly less resolution than obtained on the polarizable phases. The biphenyl phase demonstrates the best resolution of these compounds.

Similarly, the polarizable phases provide the best resolution of a series of dimethyldibenzothiophenes (Figs. 7 and 8). In this case, the 50% phenyl polysiloxane
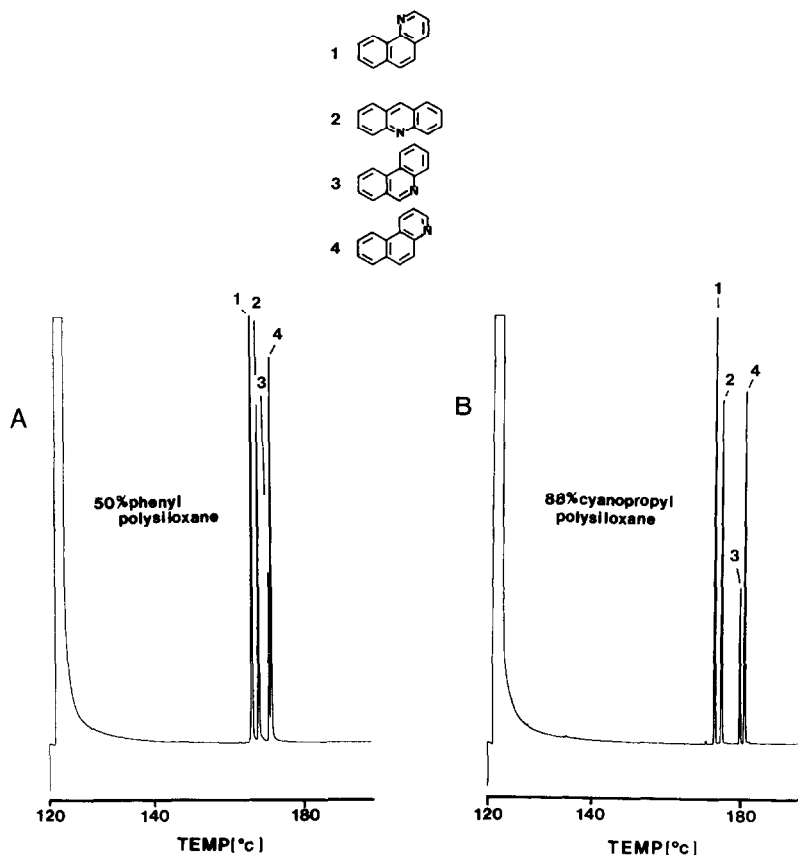
Fig. 4. Chromatograms of isomeric nitrogen heterocycles on 50% phenyl (A) and 88% cyanopropyl (B) polysiloxane stationary phases. For conditions see text.

provides nearly as good a resolution of these isomers as does the biphenyl phase.

Fig. 9 illustrates the application of the biphenyl phase to the separation of components in the most polar fraction of a coal liquid. This fraction contains mostly hydroxylated polycyclic aromatic compounds[18]. Significantly different selectivity is obtained on this phase compared to the apolar SE-54. It is interesting to note the somewhat higher elution temperatures required when the biphenyl phase is used.

A major limitation to using polar phases in GC is their increased retention of polar solutes, and the need to employ higher temperatures in order to elute them from the column. This is aggravated by the lower thermal stabilities of polar phases. Fig. 10 shows chromatograms of the same sample as analyzed in Fig. 9, except a sulfur-selective detector was used. Compounds detected in these chromatograms contained both a sulfur heteroatom and hydroxyl group. In addition to improving the resolution of mixture components, the biphenyl phase allowed the elution of a large number of higher-molecular-weight compounds that could not be eluted from the cyanopropyl phase.
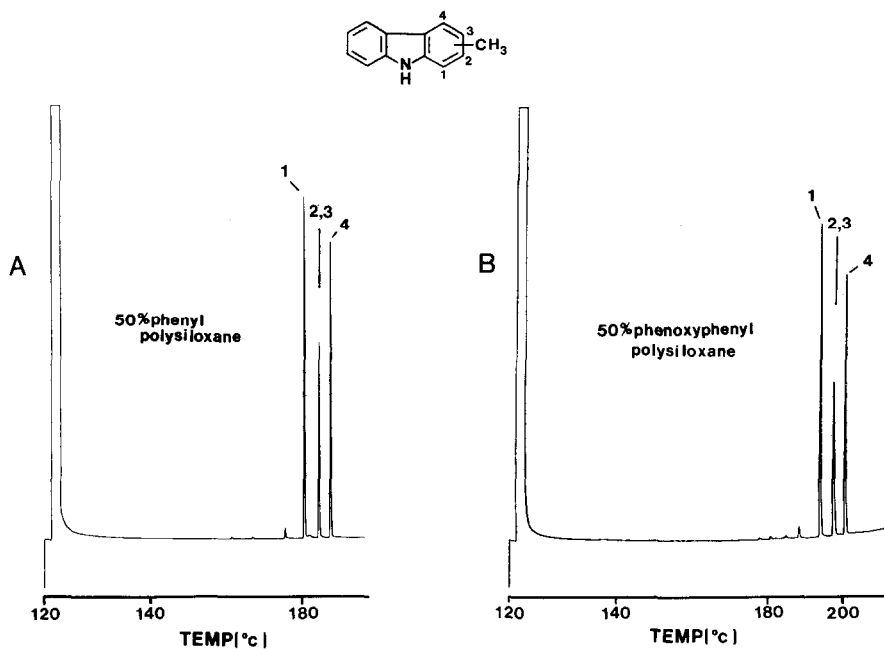
Fig. 5. Chromatograms of isomeric methylcarbazoles on 50% phenyl (A) and 50% phenoxyphenyl (B) polysiloxane stationary phases. For conditions see text.
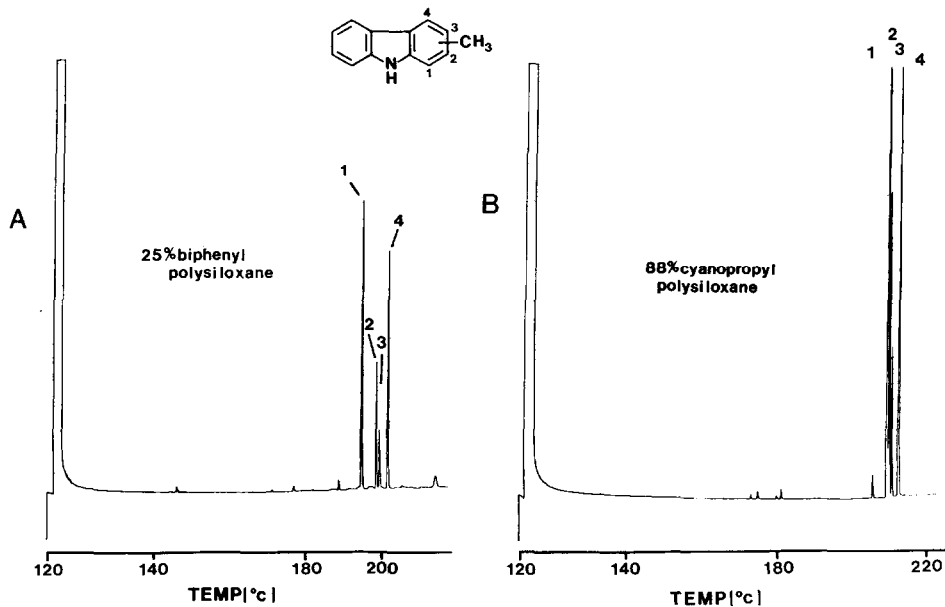

Fig. 6. Chromatograms of isomeric methylcarbazoles on 25% biphenyl (A) and 88% cyanopropyl (B) polysiloxane stationary phases. For conditions see text.
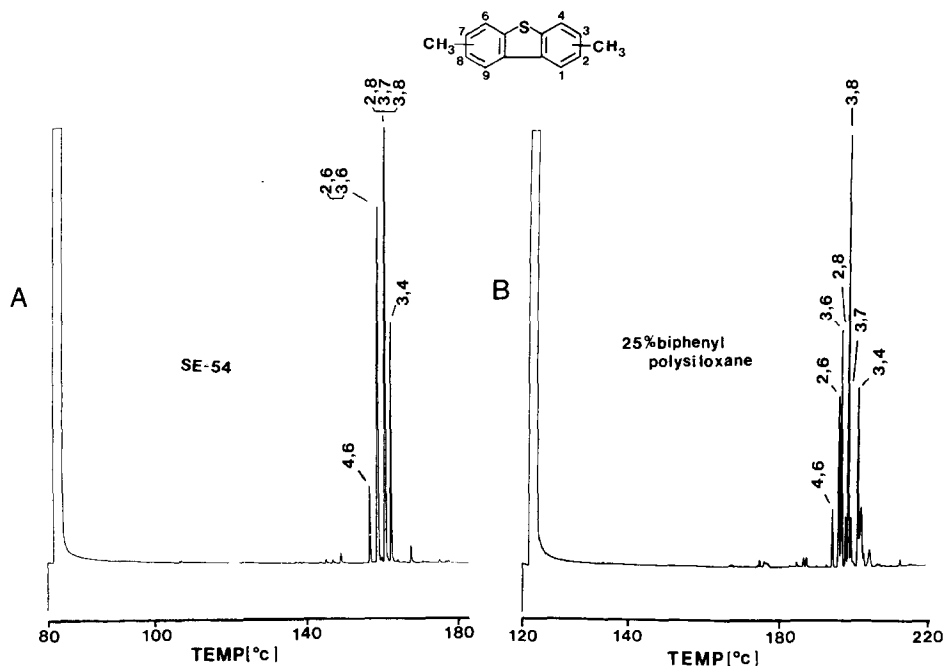
Fig. 7. Chromatograms of isomeric dimethyldibenzothiophenes on SE-54 (A) and 25% biphenyl polysiloxane (B) stationary phases. For conditions see text.
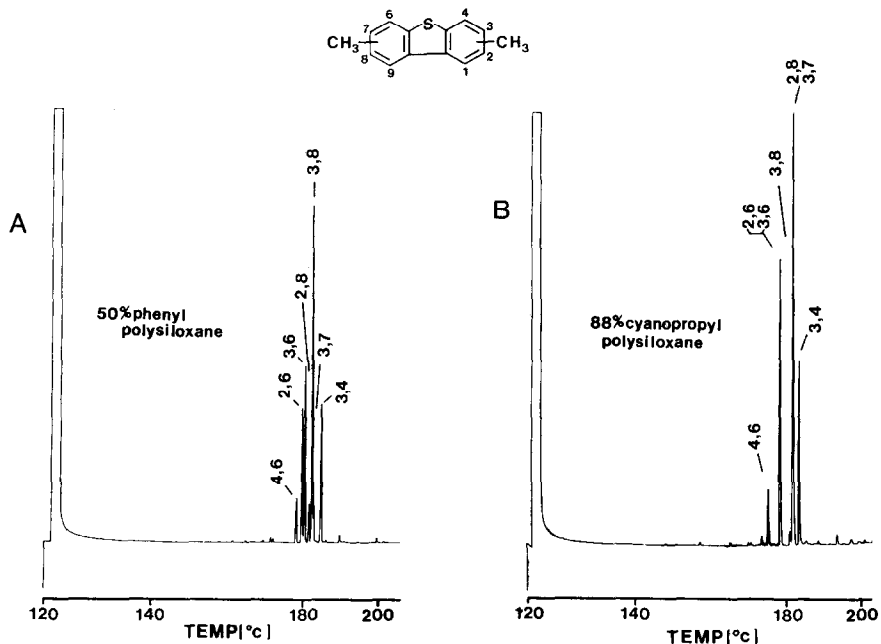

Fig. 8. Chromatograms of isomeric dimethyldibenzothiophenes on 50% phenyl (A) and 88% cyanopropyl (B) polysiloxane stationary phases. For conditions see text.
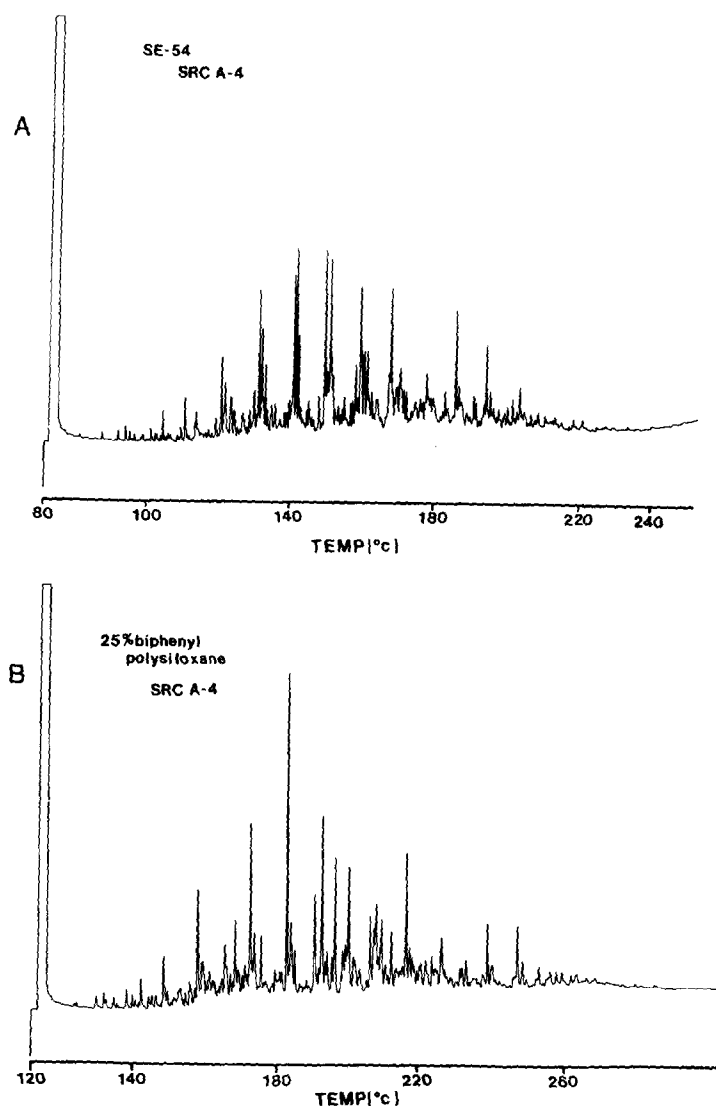
Fig. 9. Chromatograms of the hydroxylated polycyclic aromatic fraction of a solvent-refined coal liquid (SRC) on SE-54 (A) and 25% biphenyl polysiloxane (B) stationary phases. For conditions see text.

In order to compare the thermal stabilities of these phases, they were analyzed by differential scanning calorimetry in both air and nitrogen atmospheres. Both OV-1 and the phenoxyphenyl phase showed no change in composition or color at temperatures as high as 500°C under either atmosphere. The 25% biphenyl polymer showed some slight deviation from the baseline at temperatures above 260°C and a more significant change at 480°C. The analysis under an air atmosphere left the polymer slightly yellow in color. It is suspected that some impurities were not completely removed from the polymer after synthesis. In comparison, the 88% cyanopropyl
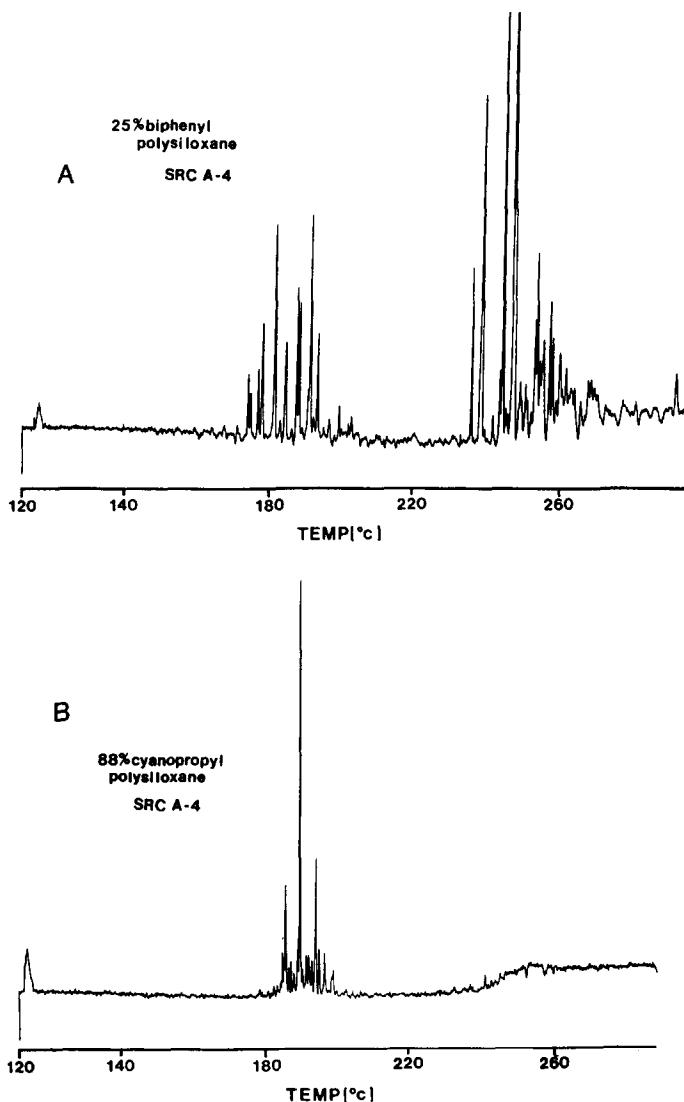
Fig. 10. Chromatograms of the hydroxylated polycyclic aromatic fraction of a solvent-refined coal liquid (SRC) on 25% biphenyl (A) and 88% cyanopropyl (B) polysiloxane stationary phases using a sulfur-selective flame photometric detector. For conditions see text.

polymer demonstrated significant deviation from the baseline at temperatures above 260°C, with major peaks at 320 and 450°C in air, and at 400 and 470°C in nitrogen. After analysis, the polymer was black in color. The susceptibility of this polymer to oxidation has previously been reported[19].

The polarizable stationary phases described here offer a number of advantages for capillary column GC. They are generally applicable to the separation of both non-polar and polar solutes. They frequently offer improved resolution of closely

related polar isomers, and they perform these separations at lower temperatures. They are thermally stable, and are resistant to oxidation. Among the polarizable phases examined in this work, the 25% biphenyl phase exhibits the best performance. The phenyl- and naphthyl-containing polymers are not as polarizable as the biphenyl-containing polymers. Although the biphenyl content could be increased above 25% by the addition of *n*-octyl groups, the resultant polymer was less thermally stable. The phenoxyphenyl-containing polymer possessed the highest polarizability and thermal stability of the polarizable phases, but demonstrated the lowest efficiency. This could be a result of the size of the functional groups and/or the high level (50%) of substitution in the polymer. A decrease in the concentration of phenoxyphenyl groups may significantly improve the mass-transfer properties of this polymer.

ACKNOWLEDGEMENT

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