POLYPHENYL ETHER SULFONES

THERMALLY STABLE POLAR PHASES FOR GAS CHROMATOGRAPHY

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SUMMARY

Stable polyphenyl ether sulfones were prepared by reacting dinuclear aromatic disulfonyl chlorides with 5- and 6-ring polyphenyl ether oligomers under Friedel–Crafts conditions. The polymers obtained are useful as high-temperature polar liquid phases in gas chromatography. Initial evaluation indicates that these phases provide good separations of hydrocarbons and sterols at column temperatures of 200–400°.

INTRODUCTION

During the past five years several new liquid phases for gas chromatography have been developed. The trend has been toward increasing both polarity and thermal stability. Polyesters and nitriles are among the most polar phases available, but few if any are usable at temperatures much above 250° and cannot be justifiably classified "high-temperature" liquid phases. Currently there are two general types of polymers amenable to use in gas–liquid chromatography (GLC) that are truly thermally stable: (1) the carborane-modified silicone fluids and (2) the polyphenyl ethers.

In 1969, Beeson and Pecsar[1] synthesized a poly-*m*-phenoxylene designed for use as a stationary phase. The concluding words of their report were: "Chemical modification of this material such as the addition of polar groups to the polymer skeleton appears as a logical extension of this work. Such modifications would enhance selectivity, but often such substitutions reduce the thermal stability of the polymers." It was therefore of interest to examine those chemical moieties by means of which the polyphenyl ether structure might be altered and to assess the effect of such modifications on the overall polymer properties. As Beeson and Pecsar aptly pointed out, the incorporation of those chemical groups normally classified "polar" usually has two adverse effects: (1) they raise the polymer melting range and (2) they reduce thermal, hydrolytic and oxidative stability. Modifications involving the introduction of hydroxyl, ester, amino or nitro groups were intuitively eliminated. Aromatic nitriles tend to trimerize at high temperatures, cross-linking the polymer and rendering it

useless for GLC. One rapidly reaches the conclusion that there exists a distinct paucity of stable substituents that may be combined to obtain polymeric liquid phases having the required degree of fluidity, polarity and heat stability.

Of the choices remaining, two were particularly promising:

(1) The aromatic ether link —thermally stable and imparts chain flexibility. It also contributes materially to a low melting range, especially when such ethers are *meta*-bridged isomeric mixtures.

(2) The aromatic sulfone link —thermally and oxidatively stable. The sulfur atom is in its highest state of oxidation and the presence of the diarylsulfone group tends to increase resonance stability along the polymer chain. The aromatic sulfones are easily prepared by Friedel–Crafts reaction with the appropriate disulfonyl chlorides.

Many types of polysulfones have been prepared in this manner in laboratories devoted to the plastics industry[2-12]. These polymers possess two major disadvantages for gas chromatographic use: (1) they normally have high softening points and (2) some contain aliphatic components. We have found that aliphatic-containing polymers generally degrade rapidly when the columns are heated much above 300°. In the interest of optimizing overall polymer properties for applications in gas chromatography, we attempted to synthesize stable, polar polyphenyl ether sulfones by coupling 5- and 6-ring polyphenyl ether oligomers with various aromatic disulfonyl chlorides via the Friedel–Crafts reaction.

EXPERIMENTAL

Equipment

Work at the Pennzoil Company Research Laboratory was done on a Barber-Coleman Series 5000 gas chromatograph equipped with a hydrogen flame ionization detector. Infrared spectra were run on a Perkin-Elmer Model 21 prism spectrophotometer. Melting ranges were determined on a Mel-temp capillary melting point apparatus. Thermogravimetric analysis (TGA) curves were run on a DuPont Thermobalance Model 990.

For the portion of this investigation conducted at the Institute for Lipid Research, Baylor College of Medicine, we utilized a Barber-Coleman Model 5000 gas chromatograph equipped with a Keithley Model 417 picoammeter, Texas Instruments recorder and a flame ionization detector. GLC conditions included: injection zone temperature, 300°; detector bath temperature, 300°; nitrogen flow-rate, 30 ml/min (at 200°); nitrogen, 22 p.s.i.; air, 40 p.s.i.; and hydrogen, 14 p.s.i. The picoammeter sensitivity was $3 \cdot 10^{-10}$ A for full-scale deflection. The mass spectrometer was an LKB 9000.

Reagents

Reagents used for the synthesis and evaluation of the polyphenyl ether sulfones were obtained as noted below. Unless specified, all were used as received.

OS-124 (a 5-ring polyphenyl ether) and OS-138 (a 6-ring polyphenyl ether) were obtained from Monsanto, St. Louis, Mo., U.S.A.

Diphenyl ether-4,4′-disulfonyl chloride (recrystallized grade) was obtained as a sample from National Polychemicals, Wilmington, Del., U.S.A.

The dimethyldichlorosilane (DMCS) used for silanizing the support material was obtained from Pierce, Rockford, Ill., U.S.A.

Nitrobenzene was procured from Aldrich, Milwaukee, Wisc., U.S.A. It was dried over 4A Linde molecular sieves and filtered prior to use.

Anhydrous sublimed ferric chloride was obtained from Matheson, Coleman and Bell, East Rutherford, N.J., U.S.A.

Antimony pentachloride was Baker Analyzed Reagent grade (J. T. Baker, Phillipsburgh, N.J., U.S.A.).

Solvents used in preparing the column packings, *i.e.* chloroform or tetrahydrofuran, were procured from Aldrich.

Column preparation

Glass W-columns (Baylor) 4 m × 3.4 mm, were silanized with DMCS. Preparation of the column packing followed our usual method[13]. The support, 80–100 mesh Gas-Chrom P, was acid-washed and silanized with DMCS prior to coating. To coat the support, 0.75 g of PZ-176 was dissolved in 100 ml of chloroform. Then 25 g of silanized Gas-Chrom P were added to the solution with swirling. A rotary-film evaporator was used for continuously mixing during the period of slow evaporation. Columns were conditioned by programming from ambient temperature to 300° at 1°/min, holding overnight at 300°, then programming from 300° to 350° at 1°/min.

The metal columns (Pennzoil) were prepared from Type 304 stainless steel, 0.125 in. O.D. × 0.062 in. I.D., from Handy and Harmon, Norristown, Pa., U.S.A. The support was 100–120 mesh Gas-Chrom Q. The polyphenyl ether sulfones were coated onto this support from a tetrahydrofuran solution. Columns were conditioned by programming from ambient temperature to 300° at 0.5–1.0°/min and then holding overnight. The columns were then further programmed to 350° or (for PZ-179) to 400° at 1°/min, the temperature being held until the baseline stabilized.

SYNTHESIS

Meta-bridged 5- and 6-ring polyphenyl ethers (OS-124 and OS-138)[14] were reacted with diphenyl ether-4,4′-disulfonyl chloride at 80° in nitrobenzene solution. Anhydrous ferric chloride or antimony pentachloride was employed as catalyst, with total reaction times varying from 8 to 24 h. Work-up yielded the polyphenyl ether sulfones as amorphous off-white solids. The mole ratios of the monomers and melting ranges of the products are given in Table I. Infrared spectra of the starting materials and of PZ-179, a typical polyphenyl ether sulfone, are shown in Fig. 1. In an idealized form, we consider PZ-179 to have the following average structure:
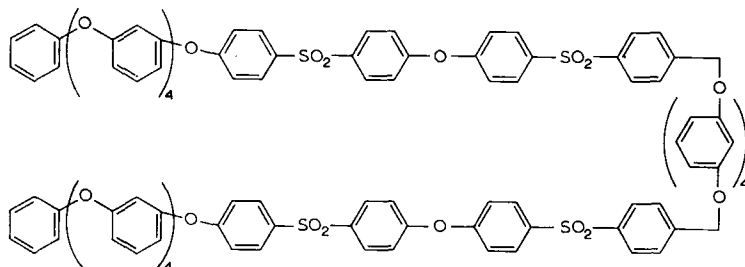
TABLE I

MOLE RATIOS OF MONOMERS AND MELTING RANGE OF PZ POLYPHENYL ETHER SULFONES

PZ	Mole ratios of monomers			Melting range (°C)
	OS-124	OS-138	Diphenyl ether-4,4'-disulfonyl chloride	
168	1.00		0.50	95–110
172	1.00		0.67	104–125
167	1.00		0.75	125–140
173	1.00		0.95	145–165
176		1.00	0.50	85–100
179		1.00	0.67	100–120

We believe that reaction occurs preferentially in the terminal ether rings and that the resulting polymers are essentially linear. There was no indication of cross-linking; all reaction products were readily soluble in a variety of common organic solvents. Table II presents a list of solubilities.

As pointed out in the literature, there are numerous other disulfonyl chlorides and aromatic substrates suitable for Friedel–Crafts polymerizations of this type. The
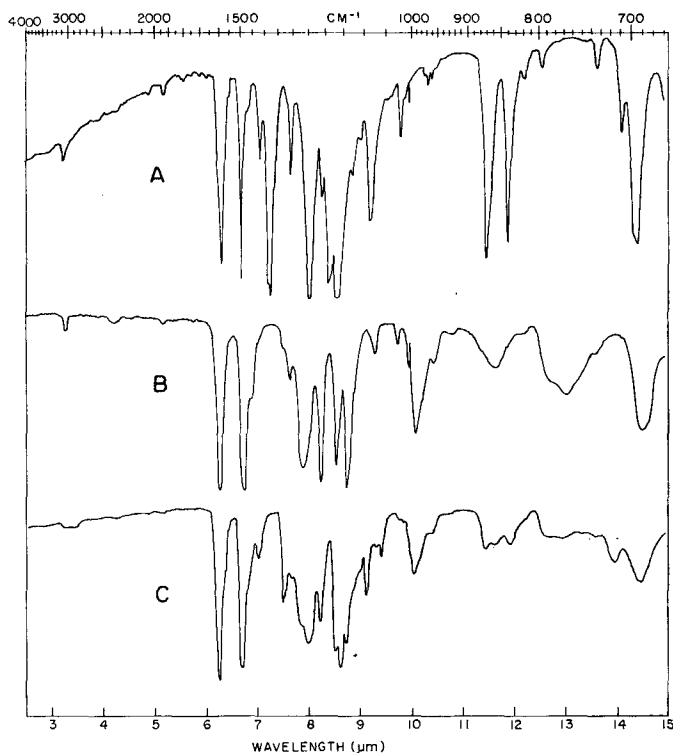

Fig. 1. Infrared spectra of diphenyl ether-4,4'-disulfonyl chloride (A), OS-138 polyphenyl ether (B), and PZ-179 polyphenyl ether sulfone (C).

TABLE II

SOLUBILITIES OF POLYPHENYL ETHER SULFONES

Soluble	Insoluble
Methylene chloride	Benzene
Chloroform	Toluene
Tetrahydrofuran	Methanol
Dioxane	Isopropanol
Dimethylformamide	Diethyl ether
Dimethylacetamide	Ethyl acetate
Dimethyl sulfoxide	Acetonitrile
Nitrobenzene	
Acetone (partially soluble)	

monomers used in this study were chosen on the basis of ease of reaction, availability and properties of the resulting polymer.

RESULTS AND DISCUSSION

From considerations of fluid operating range, volatility, and polarity, the polyphenyl ether sulfones PZ-176 and PZ-179 appear to be best. PZ-176 is usable to at least 350°. PZ-179, having a higher average molecular weight, is somewhat more stable in the 350–400° range and would probably be preferred for GLC–mass spectrometric applications. A TGA curve for PZ-179 is shown in Fig. 2.

Because PZ-176 is a solid at room temperature, as is PZ-179, a minimum operating temperature is recommended to ensure that the phase is in liquid form; this is about 200°. In view of the plethora of stationary phases already available for analyses up to 250°, no attempt was made in this study to lower the fluid range of the polyphenyl ether sulfones to temperatures of less than 200°.
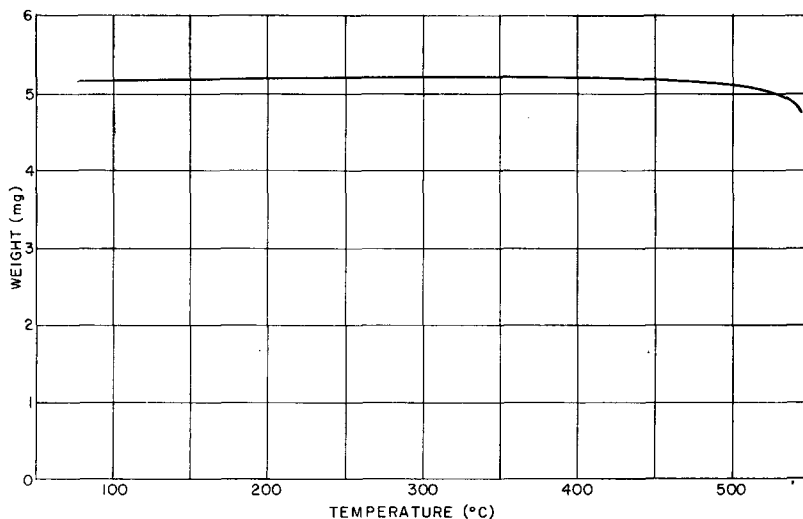

Fig. 2. TGA curve for PZ-179 polyphenyl ether sulfone. Heating rate: 10°/min in nitrogen.

Preliminary studies using PZ-176 have included separations of high-molecular-weight *n*-alkanes, fatty acid methyl esters, isomeric cholestanols and various sterols as the trimethylsilyl (TMS) ethers. PZ-179 has been initially evaluated for analyses of aromatic hydrocarbons, waxes, and some pesticides. The polar nature of PZ-176 leads to the selective retention of compounds containing carbon–carbon unsaturation, hydroxyl groups, ketone groups and carboxylic ester groups. The degree of polarity is much greater than that observed for OV-17 (phenyl methyl siloxane polymer) and is comparable to some polyester phases.

The combination of polarity and stability observed for this phase suggests that it should be evaluated for all current applications involving temperatures above 200°.

Column bleed

Fig. 3 shows the bleed-rate observed for a 4 m × 3.4 mm glass column of 3% PZ-176 on silanized 80–100 mesh Gas-Chrom P. Curve A is the bleed after conditioning the column overnight at 300° and then programming once from 300° to 350° at 1°/min. Curve B is the bleed after four days of use between 200° and 330°. The column bleed continued to drop during use.
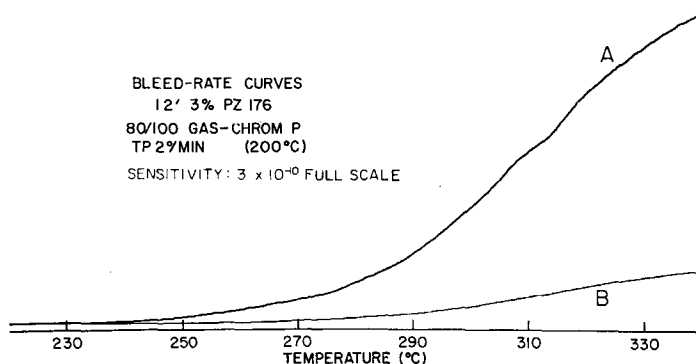

Fig. 3. Bleed-rates of 3% PZ-176 column (4 m × 3.4 mm glass). Curve A: conditioned overnight at 300°, then programmed from 300° to 350° at 1°/min. Curve B: bleed-rate after 4 days of use at 200–330°. A picoammeter sensitivity of $3 \cdot 10^{-10}$ A for full-scale deflection was used.

Background ions in mass spectrometry

A 4 m × 3.4 mm glass column of 3% PZ-176 on silanized 80–100 mesh Gas-Chrom P was used with an LKB 9000 mass spectrometer to determine the background ions attributable to the liquid phase. At 350° eight ions, listed in order of decreasing intensity were found: *m/e* 186, 94, 77, 96, 115, 78, 129, 157. At 300°, the background was negligible with only very low intensities of ions at *m/e* 186, 94, 77 and 78. Several ions attributable to the silicone septum were also present. In order of decreasing intensity, they included *m/e* 207, 281, 341, 73 and 147 (ref. 15). A new injector was devised to decrease by 50% the intensity of these interfering ions.

Thermal stability under mass spectrometric conditions

A small sample of PZ-176 was heated in the probe assembly of a CH7 mass

spectrometer. The chief background ions noted above became evident as weak peaks at 350–400°.

Polarity studies

A series of separations was carried out by temperature programming in order to determine the degree of polarity of PZ-176.

McReynolds constants[16] are frequently used to define the relative polarity of liquid phases. The compounds normally used to determine retention behavior include rather volatile liquids, such as benzene, butanol, 2-pentanone, nitropropane and pyridine. The new polar phase PZ-176 does not form a completely liquid film below 200°. At this temperature, the retention times of low-molecular-weight compounds essentially converge.

Rather than suggest a new series of compounds for characterizing high-temperature phases, we chose to examine the polar nature of PZ-176 by direct examination of several mixtures of compounds of rather low volatility. Most of the mixtures contained compounds of varying polarity.

n-Alkanes

n-Alkanes elute as trailing peaks if the initial temperature is much below 200°. This limits the use of the phase to compounds having methylene unit (MU) values above 26. No difficulty is experienced in eluting n-tetratetracontane (around 330° on 4 m, 3 % column) provided a sufficiently high injector temperature is used and no cool zones are present along the chromatographic pathway (see Fig. 4). Fig. 5 shows a typical programmed analysis of hydrocarbon wax.
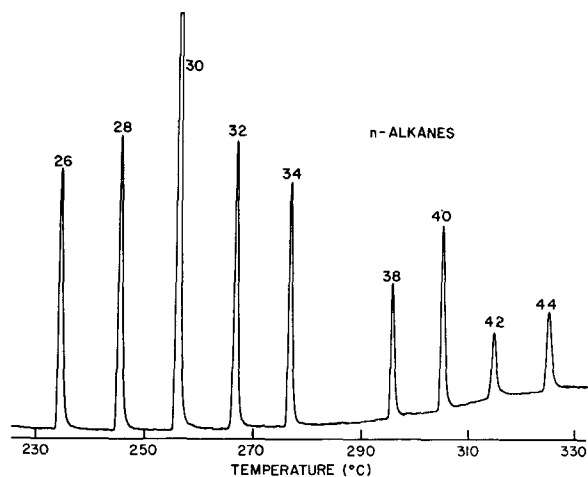

Fig. 4. Elution of n-alkanes: 4 m × 3.4 mm glass column; 3 % PZ-176 on 80–100 mesh silanized Gas-Chrom P temperature programmed 2°/min from 200°.

Aromatic hydrocarbons

Polynuclear aromatics are eluted easily from the polyphenyl ether sulfone columns. Fig. 6 presents a typically programmed run.
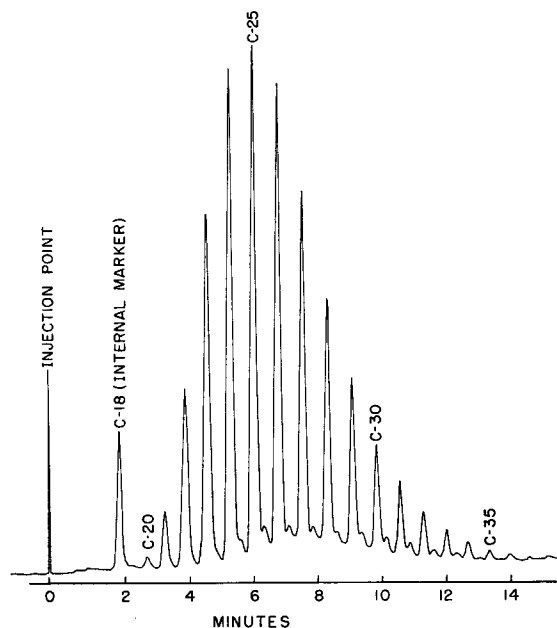
Fig. 5. Elution of hydrocarbon wax. Column: 10 ft. × 1/8 in. O.D. stainless steel; 10% PZ-179 on 100–120 Gas-Chrom Q. Programmed from 200° to 350° at 10°/min. Pressure: 30 p.s.i. helium.

Fatty acid methyl esters

The polar nature of PZ-176 is reflected in the order of elution of saturated and unsaturated fatty acid methyl esters. For any related pair $C_nH_{2n}O_2/C_nH_{2n-2}O_2$, the unsaturated compound elutes after its saturated partner. Multiple unsaturation increases the retention time as demonstrated by the series: methyl stearate, methyl oleate, methyl linoleate, methyl linolenate. Table III includes MU values for the methyl esters of fatty acids along with corresponding values determined on a 12-ft. column
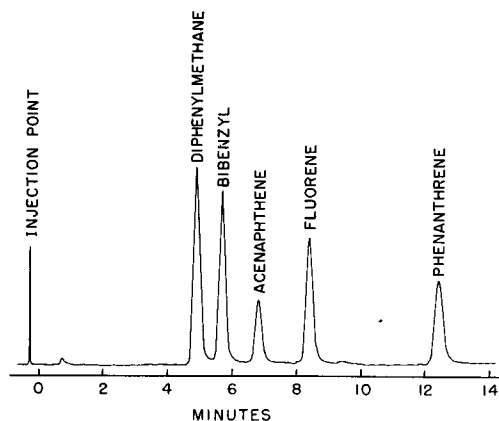

Fig. 6. Separation of aromatic hydrocarbons. Column: 10 ft. × 1/8 in. O.D. stainless steel; 10% PZ-179 on 100–120 Gas-Chrom Q. Programmed from 200° to 350° at 10°/min. Pressure: 30 p.s.i. helium.

TABLE III

MU VALUES FOR FATTY ACID METHYL ESTERS PROGRAMMED 2°/MIN

Methyl ester	3% PZ-176*	1% SE-30**
Stearate	23.96	21.06
Oleate	24.15	20.77
Linoleate	24.60	20.77
Linolenate	25.14	20.69
Arachidate	26.04	23.07
cis-11-Eicosenoate	26.27	22.80
Behenate	28.11	25.17
Erucate	28.35	24.82
Lignocerate	30.24	—
Nervonate	30.47	26.84

* Initial temperature, 175°.
** Initial temperature, 150° (ref. 17).

of 1% SE-30. These values are about 3 units higher on the PZ-176 column than on the SE-30 column.

Cholestanes

Baseline separation was achieved for the 5β-cholestane (MU = 32.25)/5α-cholestane (MU = 32.89) pair. The theoretical plate efficiency of the column was initially 5000 (based on 5α-cholestane eluted isothermally at 250°). After a month of constant use this value was 4000.

Cholestanols

The retention behavior exhibited by various sterols and related compounds on 3% PZ-176 demonstrates the polar nature of this phase (see Table IV). A comparison of MU values from 1% SE-30 (ref. 17) and 3% PZ-176 indicates a positive shift on PZ-176 of about 5 units for 5β-cholestane and 5α-cholestane, about 11 units for 5β-cholestan-3β-ol, 5α-cholestan-3α-ol, 5β-cholestan-3α-ol and 5α-cholestan-3β-ol, and a shift of about 13 units for 5α-cholestan-3-one. Evidently, the phase has a greater affinity for the carbonyl function than for the hydroxyl group. On 3% PZ-176 the

TABLE IV

MU VALUES FOR STEROLS AND RELATED COMPOUNDS ON SEVERAL PHASES

Compound	3% PZ-176*	1% SE-30*	1% OV-1*	3% PZ-176**	1% OV-17	1% Dexsil 300 GC**	1% SE-30**
5β-Cholestane	32.25	27.55	27.18	—	28.53*	—	—
5α-Cholestane	32.89	27.90	27.50	—	28.94*	—	—
5β-Cholestan-3β-ol	40.03	30.00	—	33.13	31.10**	30.72	30.28
5β-Cholestan-3α-ol	40.63	30.00	—	34.09	31.29**	31.10	30.40
5α-Cholestan-3α-ol	40.83	30.00	—	33.45	31.23**	30.80	30.36
5α-Cholestan-3β-ol	41.47	30.43	—	35.15	32.37**	31.77	31.19
5α-Cholestan-3-one	43.34	30.69	—	—	—	—	—

* Underivatized compound(s).
** TMS derivative(s).

total range for chromatographic separation of these compounds extends over about 11 methylene units, whereas on 1% SE-30 the range is only about 2.5 units.

That PZ-176 is sensitive to the molecular geometry of the compounds being separated is reflected in ΔMU for the pair 5β-cholestane/5α-cholestane. Values of ΔMU decrease in the order: 0.64 on 3% PZ-176 $\gg$ 0.41 on 1% OV-17 $>$ 0.35 on 1% SE-30 $>$ 0.32 on 1% OV-1.
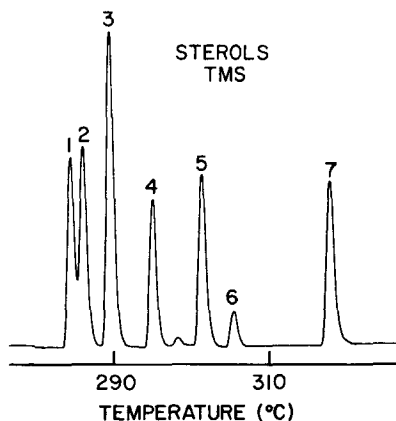

Fig. 7. Separation of four isomeric cholestanols and related sterols as TMS ethers on a 4 m × 3.4 mm glass W-column of 3% PZ-176 on silanized 80–100 mesh Gas-Chrom P temperature programmed at a rate of 2°/min from 200°: (1) 5β-cholestan-3β-ol, (2) 5β-cholestan-3α-ol, (3) 5α-cholestan-3α-ol, (4) 5α-cholestan-3β-ol, (5) stigmasterol, (6) β-sitosterol and (7) cholesteryl butyl ether.

Fig. 7 shows a separation of four isomeric cholestanols as TMS ethers (1–4) plus (5) stigmasterol (TMS; MU = 36.31), (6) β-sitosterol (TMS; MU = 37.13), and internal reference compound (7) cholesteryl butyl ether (MU = 39.50). The TMS ethers[18], which have much less polar character than the underivatized compounds, have lower MU values (by about 7 units) and allow geometric effects to be significant as reflected by a change in the order of elution. Of the four phases, PZ-176, OV-17, Dexsil 300 GC and SE-30, only PZ-176 successfully separates all four isomeric cholestanol TMS ethers. Table IV indicates an order of decreasing phase polarity: PZ-176 > OV-17 > Dexsil 300 GC > SE-30.

CONCLUSIONS

(1) The Friedel–Crafts synthesis of several special-purpose polyphenyl ether sulfones has been completed. Two of these polymers, PZ-176 and PZ-179, have undergone evaluation for use as high-temperature polar liquid phases in gas chromatography. The low volatility of PZ-179 in the 350–400° range suggests application in GLC–mass spectrometry.

(2) The polyphenyl ether sulfones contain no silicon or other constituents which would leave inorganic residues in the detectors.

(3) As part of a continued study, it is proposed to evaluate the polyphenyl ether sulfone polymers on both metal and glass capillary columns.

(4) The polyphenyl ether sulfone phases have proven useful for separations involving a wide variety of compounds. Their thermal stability and polarity suggest further evaluation in analyses requiring temperatures above 200°.

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