Note

Stationary phase properties of cyanophenyl ethers

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The majority of low-molecular-weight substances used as stationary phases in gas chromatography (GC) are restricted by their volatility to operation at fairly low temperatures. For the separation of involatile compounds at temperatures above 250°C, polymeric materials are invariably used. In fact, most separations in the modern literature are performed using polymeric materials. These stationary phases have one principal disadvantage: variable composition from batch to batch and further alterations in molecular weight distribution by the selective evaporation of low-molecular-weight oligomers upon column conditioning. These materials are not suitable as reference stationary phases for GC.

Squalane has long been used as a non-polar reference phase in GC. Riedo *et al.*[1] prepared a synthetic hydrocarbon with an upper temperature limit of 280°C, which is a suitable replacement for the more volatile squalane. The *meta*-linked phenyl ethers containing five, six or seven phenyl rings have been used in GC to separate a wide range of samples, and are suitable for use as moderately polar reference stationary phases[2-5]. A property of the phenyl ethers, useful for GC, is their wide liquid range with a high maximum upper operating temperature. An unusual feature for such low-molecular-weight materials. For example, the six-ring phenyl ether has an upper temperature operating limit of 250°C. In an attempt to prepare thermally stable polar reference phases we have investigated several reactions for the site-specific introduction of polar substituents into the phenyl ether backbone[6,7]. A compound synthesized during these studies, 1,3-dicyano-4,6-bis[2,4-dicyano-5-(4-cyanophenoxy)phenoxy]benzene (Fig. 1) is evaluated as a polar stationary phase in this paper.
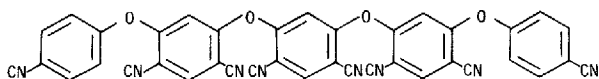

Fig. 1. Structure of the cyanophenyl ether phase 1,3-dicyano-4,6-bis[2,4-dicyano-5-[4-cyanophenoxy)-phenoxy]benzene, PPE-4.

In related studies, Mathews *et al.*[8] have described the preparation of poly-phenyl ether sulfones by copolymerization of five- and six-ring phenyl ethers with diphenyl ether-4,4′-disulfonyl chloride. These materials are useful polar stationary phases with an operating temperature range of 200–400°C[8-17]. However, they are

polymers of undefined molecular weight and are, therefore, unsuitable as a reference stationary phase.

EXPERIMENTAL

4,4′-Dicyanophenyl ether (DPE-4) and 1,3-dicyano-4,6-bis[2,4-dicyano-5-(4-cyanophenoxy)phenoxy]benzene (PPE-4) were prepared as described previously[7]. Column packings containing 2–20% (w/w) of PPE-4 on Chromosorb W AW or P AW were prepared by the rotovapor technique using isopropanol as solvent for the stationary phase.

Equipment
For GC a Varian 3700 gas chromatograph with flame-ionization detectors was used. Glass or nickel columns of various lengths and internal diameters were used during this study. For details see Table I and Figs. 2 and 3. Oxygen-free nitrogen was used as carrier gas.
For the determination of copper concentrations a Varian Techtron 1100 atomic absorption spectrometer was used.

Stationary phase digestion
A weighed sample of DPE-4 or PPE-4 (≈ 1 g) was dissolved by adding a mixture of concentrated nitric and sulfuric acids (3:1) and gently heating the mixture to reflux in a conical flask. When completely dissolved the sample was cooled and diluted with water to 50 ml. Copper standards were prepared from the metal in an identical manner.

RESULTS AND DISCUSSION

The primary properties which characterize a stationary phase are its minimum and maximum operating temperature, its polarity or selectivity determined by measuring McReynolds' constants, and the efficiency of columns prepared using the phase compared to values normally obtained for other phases or predicted by theory.

Minimum column operating temperatures
PPE-4 is a solid at room temperature softening at about 72–73°C and finally melting at 90–91°C. Its minimum operating temperature as a stationary phase was determined from a plot of column efficiency *vs.* column operating temperature (Fig. 2). The column temperature was raised in increments of 10°C, starting at 90°C, and the column plate count calculated for an appropriate *n*-hydrocarbon having a capacity factor value in the range 15–20. The column efficiency reaches a plateau value at about 140°C, and this is taken to be the minimum operating temperature for PPE-4. The plate count obtained was lower than expected being about 75% of the value obtained for otherwise identical columns prepared from SE-30 and Carbowax 20M. This value was influenced, to some extent, by the method of column conditioning (see later) and also by the coating technique used to prepare the packing. PPE-4 is light yellow in color and visual inspection of the packings obtained when methanol, ethanol, ethyl acetate, acetone, toluene, and chloroform were used as the solvent for the
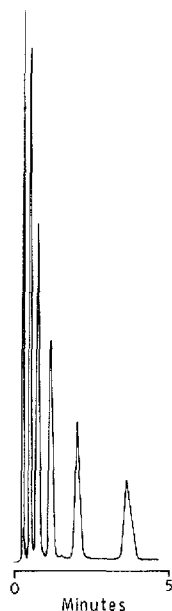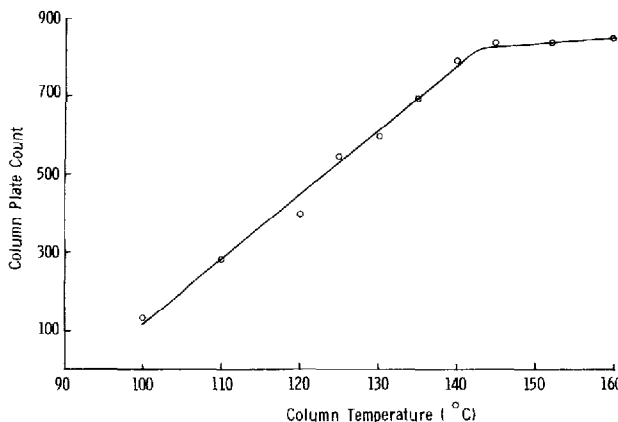
Fig. 2. Plot of plate count *vs.* column operating temperature for *n*-hydrocarbons having K values between 15 and 20. Column: 3 ft. × 0.25 in. I.D., 10 % PPE-4 on Chromosorb P AW, 80–100 mesh. Nitrogen flow-rate: 40 ml/min.

Fig. 3. Separation of a mixture of C_7–C_{12} *n*-hydrocarbons on a 2 m × 0.125 in. I.D. nickel column, 10 % (w/w) PPE-4 on Chromosorb W AW, 80–100 mesh. Column temperature: 140°C. Nitrogen flow-rate: 19 ml/min.

stationary phase clearly indicated an uneven distribution of phase throughout the support. Propanol or isopropanol gave an even distribution of phase, and yielded columns of superior efficiency. The separation of a mixture of hydrocarbons on a typical column is shown in Fig. 3.

Determination of McReynolds' constants

Squalane is not stable at the minimum operating temperature of PPE-4. To obtain approximate McReynolds' constants SE-30 was used as a non-polar reference phase. Compared to the normal method of calculating McReynolds' constants the values given in Table I are probably slightly larger than they would otherwise be[18]. For relative purposes they do indicate that PPE-4 is a polar phase of similar selectivity to the cyanopropylsiloxane phases.

Determination of maximum column operating temperature

The upper temperature operating limit was established by temperature programming and long term isothermal column conditioning for periods in excess of 12 h. PPE-4 does not behave in a manner similar to most stationary phases. The column is stable to long term conditioning at 200°C, and this seems to be the safe upper operating temperature limit. At 220°C, column conditioning for periods longer than 12 h does not show any change in capacity factor values for test probes but peak

TABLE I

DETERMINATION OF McREYNOLDS' CONSTANTS

Columns were 12 ft. × 0.125 in. I.D., 10 % (w/w), loading on Chromosorb W AW, 100–120 mesh. Column temperature: 140°C. Nitrogen flow-rate: 25 ml/min.

Test probe	Retention index value on PPE-4	Retention index value on SE-30	Difference in retention index values
Benzene	1080	638	442
n-Butanol	1188	592	596
2-Pentanone	1167	631	536
1-Nitropropane	1363	654	709
Pyridine	1492	722	770
2-Methyl-2-pentanol	1152	696	456
2-Octyne	1056	839	217
1,4-Dioxane	1261	700	561
cis-Hydrindane	1200	600	600

symmetry factors start to deteriorate compared to columns conditioned at lower temperatures. At higher temperatures both retention and resolution is severely affected.

The performance of the column deteriorates at temperatures higher than 200°C due to *in situ* polymerization. Inspection of the column packing material after conditioning at 250°C shows the presence of an uneven distribution of hard resinous nodules. Unlike PPE-4 this material is largely insoluble in most organic solvents. The soluble portion of this material behaves very differently to unheated PPE-4 on analysis by high-performance liquid chromatography. Rather than a single sharp peak a broad hump with no clearly defined retention volume was obtained. This cross-linking reaction is not induced by the support, as sealing a sample of PPE-4 into a melting point tube and heating it to 250°C for 24 h reveals the same result. The most likely explanation for the above observations is the thermal induction of cross-linking between the aromatic cyano groups on different molecules. The cross-linked polymeric material is hard, resinous, and thermally stable to temperatures in excess of 350°C, but has no useful stationary phase properties. The model compound DPE-4 was also found to show similar properties indicating that aromatic cyano compounds in general may make poor high-temperature stationary phases.

It is known that aromatic cyano compounds in the presence of certain metal salts, *e.g.*, copper, can form metal-containing polymers of high molecular weight by heating to temperatures in excess of 200°C[19–21]. PPE-4 and DPE-4 are prepared by reaction of the bromo analogue with cuprous cyanide, and in the case of PPE-4, the decomposition of the PPE-4 copper complex could only be achieved with difficulty[7]. Atomic absorption measurements indicated that PPE-4 contained 0.095 % (w/w) of copper. This corresponds to 1 g atom of copper to every ≈ 100 g moles of PPE-4. This is too large a ratio to explain the stationary phase behavior in terms of the formation of copper cyanine polymers[19,20]. Also, DPE-4 which did not contain copper in detectable quantities, was found to cross-link under reaction conditions similar to those observed with PPE-4.

CONCLUSIONS

PPE-4 can be used as a polar stationary phase in GC over the temperature range 140–200°C. Although meeting all chemical and structural requirements for a standard polar phase its chromatographic properties fall short of those desired. However, PPE-4 is a useful intermediate from which other polar stationary phases containing a high concentration of polar side chain groups at specific molecular sites can conveniently be prepared.

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