

CHROM. 6924

## AROMATIC HYDROCARBON STATIONARY PHASES FOR GAS-LIQUID CHROMATOGRAPHY

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(Received May 7th, 1973)

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### SUMMARY

The performances of Apiezon L and linear polystyrene as gas chromatographic stationary phases have been examined and compared. A new non-polar stationary phase, poly( $\alpha$ ,4-benzyl) has been synthesized and its performance evaluated. Apiezon greases can be replaced as stationary phases by the polymeric compounds which are of known structure and superior separating efficiency. The recommended working temperature ranges are, polybenzyl up to 240°, polystyrene 240–340°.

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### INTRODUCTION

The Apiezon greases have been used successfully as stationary phases for many years. Their widespread use is due partly to their wide range of operating temperature, and also to the fact that efficient column packings may be prepared which are capable of good resolution of chromatographic peaks. The disadvantage of the Apiezons is that their structure is unknown, therefore the magnitude of solute-solvent interactions cannot be measured. The ratios of the many constituents will vary from batch to batch so that reproducible columns cannot be prepared (theoretically) from different batches of material. Suppliers<sup>1</sup> describe the Apiezons as hydrocarbons with "high contents of terminal methyl groups, unsaturated methylene side-chains, branched-chain structures, *trans*-substituted double bond linkages and high contents of benzene nuclei". Another disadvantage of the Apiezon greases now becomes apparent: conditioning of a freshly prepared Apiezon column at different temperatures will result in differing amounts of stationary phase being lost during the process. Gerrard *et al.*<sup>2</sup> have shown how the loss of Apiezon L stationary phase as a function of temperature is dependent on the history of the column packing. As the Apiezons are complex mixtures however, the more volatile ingredients will be removed on conditioning. These are more likely to be paraffinic and olefinic moieties than benzenoid, so the benzenoid content of the stationary phase will be a function of column conditioning temperature. As the delocalised electrons of the aromatic system contribute to gas-liquid chromatographic (GLC) retention by dipole-induced dipole interactions with solutes, this leads to the very unsatisfactory

state that retention parameters on Apiezon columns will depend on both origin and nature of conditioning of the stationary phase.

The first attempt at replacing Apiezon by an aromatic hydrocarbon of known composition was the introduction of benzyldiphenyl. This is an excellent stationary phase but has a severely limited working range of 80–150°. Diphenyl itself can function from 71°, its melting-point, but will have a lower maximum working temperature than benzyldiphenyl. *p*-Terphenyl and *p*-quaterphenyl, with melting-points of 171° and 320°, respectively, would be quite unsuitable as stationary phases.

Linear polystyrene, coated onto a suitable support, should be capable of acting as a stationary phase above 110°, where the polymer exhibits a glass to rubber transition, and should be thermally stable to high temperatures above which polymer chain unzipping would produce monomeric styrene. Cross-linked polystyrene beads (Porapak) are finding use in GLC separations<sup>3,4</sup> both in the coated and uncoated forms, but the properties of linear polystyrene as a phase in "gas-rubber chromatography" have not previously been examined. The reason for this is presumably the very high viscosities exhibited by rubbers. The viscosity features in the mass transfer term of the Van Deemter equation<sup>5</sup>: high stationary phase viscosity leads to a high mass transfer coefficient resulting in peak broadening with subsequent loss of resolution in the separation of mixtures. One way of reducing the viscosity of the polymer would be to incorporate a plasticizer. The possible uses of polystyrene, plasticized and unplasticized, are discussed in this paper.

The ideal aromatic hydrocarbon stationary phase must exhibit a wide working range of temperature, have a low melting-point and low viscosity above the melting-point, be non-volatile, thermally stable, be capable of production as a pure compound of known composition and be economical to manufacture. Such a rigorous specification is difficult to meet but not impossible. The polyphenyl melting-points are high due to conjugation: the benzyldiphenyl melting-point is only 9° higher than diphenyl itself as the additional benzyl group does not extend the conjugation. Benzyldiphenyl however, is too small a molecule so the volatility aspect precludes its use above 150°. If five or six benzene rings could be linked through methylene groups to give a pure product, a polybenzyl, the substance would conform to the specification given above. This paper describes the synthesis of such a poly( $\alpha$ ,4-benzyl) and discusses its properties in comparison with Apiezon L and linear polystyrene.

## EXPERIMENTAL

The instrument used in this work was a Pye Series 104 gas chromatograph with a flame ionization detector. All columns were 1 m  $\times$  6 mm O.D. stainless-steel tubing, packed with 10% (w/w) stationary phase coated on a Chromosorb W, acid-washed, DCMS-treated support. The stationary phases examined were Apiezon L, poly( $\alpha$ -4-benzyl), polystyrene and a plasticized polystyrene where the support was coated with 8% (w/w) polystyrene + 2% (w/w) Apiezon L. All polystyrene was dissolved in dioxan and precipitated by methanol as an initial clean-up step.

### *Preparation of poly( $\alpha$ ,4-benzyl)*

(a) *p*-Di(bromomethyl)benzene. Reflux 53 g of *p*-xylene and 300 ml of carbon tetrachloride in a 1-l flask irradiated by ultraviolet light. Add 160 g of bromine over a

period of 1 h maintaining reflux until the bromine coloration has disappeared completely. Allow to cool overnight, then filter the crystallised *p*-di(bromomethyl)-benzene (care is required as the product is extremely lachrymatory).

(b) *Poly(α,4-benzyl)*. To 50 g of diphenylmethane and 52 g of stannic chloride add a solution of 26.4 g *p*-di(bromomethyl)benzene in 100 g of diphenylmethane with stirring. Maintain the stirring for 5 h at room temperature, then allow to stand overnight. Pour the reaction mixture into 500 ml of 10% sulphuric acid, stir for at least 1 h, then reject the aqueous phase. Repeat the washing procedure twice to ensure complete removal of tin, wash finally with 500 ml of water. Distill under reduced pressure to remove excess diphenylmethane (b.p. 140° at 22 mm). Then extract the residue (a red oil) with boiling ethanol. *Poly(α,4-benzyl)* crystallises as a white compound on cooling the ethanol (m.p. 116°, yield from the Friedel-Crafts reaction 50%). Extraction of the ethanol-insoluble residue with boiling butanol gives, on cooling, an amber grease with a softening point of 43° (drip point from thermometer bulb). This grease consists exclusively of higher polybenzyls and has a chromatographic working range of 50–240° as a stationary phase.

Thermogravimetric measurements on column packings were carried out on a thermal balance with the sample in an atmosphere of nitrogen, flow-rate 100 ml/min. Rate of temperature increase, 2°/min.

Column efficiencies and HETP values were obtained at a constant nitrogen flow-rate of 20 ml/min using six aromatic hydrocarbons each being used to determine the efficiency at an oven temperature corresponding to its boiling-point. The six hydrocarbons, and working temperatures used, were toluene (110°), *p*-xylene (137°), propylbenzene (158°), *n*-butylbenzene (180°), naphthalene (218°) and diphenylmethane (261°).

#### *Stationary phase efficiency for the resolution of mixtures*

Although the procedure followed for packing the columns was standardised as far as possible, each column contained a different number of theoretical plates as determined from the *n*-butylbenzene peak obtained at a column temperature of 180° and flow-rate 20 ml/min. The efficiency of the liquid phase itself was therefore assessed for the following two-component mixtures: decane–dodecane, mesitylene–*n*-butylbenzene, benzaldehyde–acetophenone, methyl benzoate–isoamyl butyrate, nitrobenzene–*p*-nitrotoluene and benzyl alcohol–cyclohexanol. This assessment was made using the Purnell<sup>6,7</sup> formula

$$n_{req.} = 16R^2 \left( \frac{\alpha}{\alpha - 1} \right)^2 \left( \frac{k + 1}{k} \right)^2$$

where  $k$  is the partition ratio =  $t'_R/t_m$  for the second peak and  $\alpha$  is the relative retention =  $k_2/k_1$ .

The number of theoretical plates required for unit resolution at 180° was thus obtained.

#### *Retention indices*

Retention indices for *n*-butylbenzene, acetophenone, methyl benzoate, nitrobenzene and aniline at 180° and flow-rate 20 ml/min were obtained using Apiezon L,

polystyrene and polybenzyl columns, the sample being chromatographed with the two appropriate *n*-paraffins and the Kováts<sup>8</sup> formula applied to the corrected retention times.

## RESULTS AND DISCUSSION

The thermograms (Fig. 1) showed that while the percentage loss of stationary phase was 5% at 200° and 10.4% at 300° for Apiezon L, polystyrene was thermally stable to 340° and polybenzyl to 250°.

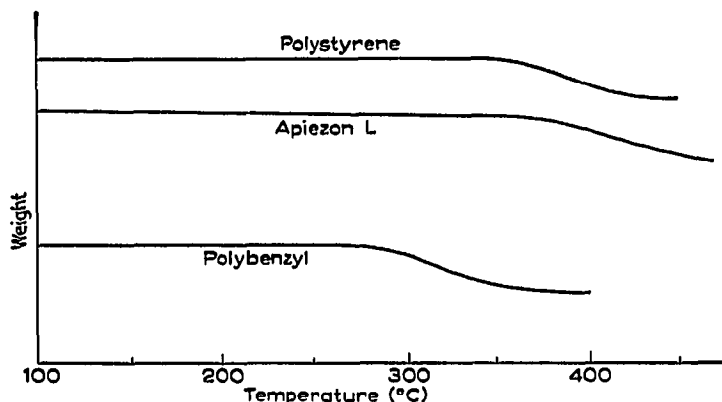
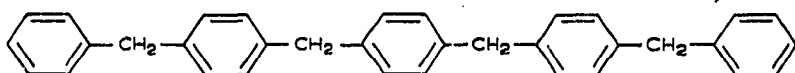


Fig. 1. Thermograms of column packings, 10% (w/w) stationary phase on Chromosorb W.

Elemental analysis and a molecular weight of 448 (theory, 438) determined ebullioscopically confirm that polybenzyl is:



the mild Friedel-Crafts catalyst, stannic chloride, being used to ensure *para* substitution.

The ethanol-insoluble, butanol-soluble portion with a melting-point of 43°, gave a molecular weight of 795 and will consist of a mixture of two higher polybenzyls: (a) condensation of polybenzyl with *p*-di(bromomethyl)benzene and diphenylmethane, molecular weight 708; and (b) condensation of two molecules of polybenzyl with one molecule of *p*-di(bromomethyl)benzene, molecular weight 978. This mixture is also thermally stable to 250°.

Fig. 2 shows a comparison of the theoretical plate heights of the four columns when efficiencies are determined on aromatic hydrocarbons at their boiling-points. The standard value, benzene at 80°, has been included for Apiezon L. Polybenzyl and Apiezon L are thus seen to give similar values for the height equivalent to a theoretical plate (HETP) over the polybenzyl working range of 116–240° when coated on similar supports and column packing is carried out in a standardized manner. The predicted effect of high viscosity leading to low efficiency in polystyrene

columns is apparent in the temperature range 110–200°. The effect of plasticizer on the polystyrene to increase efficiency is also as expected. This increase however, is too small to render polystyrene a suitable stationary phase below 200°. Above 220°, the efficiencies of polystyrene and Apiezon L are comparable, in fact, by 261° the polystyrene is exhibiting the higher efficiency.

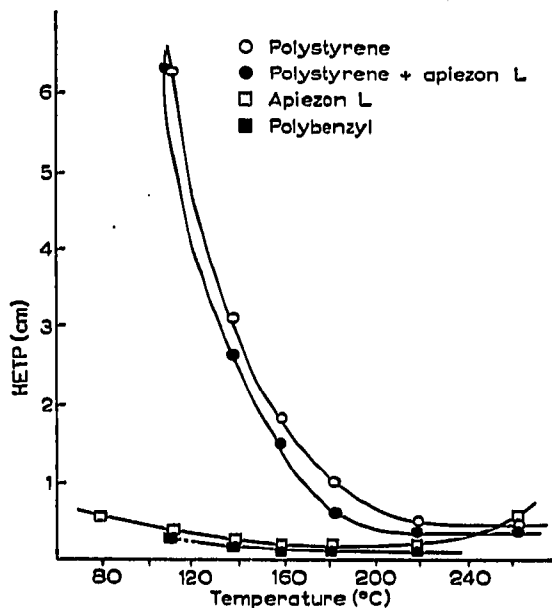


Fig. 2. Variation of HETP with temperature, determined using aromatic hydrocarbons.

The results from Figs. 1 and 2 would indicate that polybenzyl and polystyrene are complementary stationary phases. For work in the region 50–240° the higher polybenzyl grease is suitable whilst for separation in the 240–340° region, polystyrene is the preferred stationary phase. For work involving a knowledge of the actual structure of the stationary phase, polybenzyl itself is the preferred phase in the working range 116–240°.

The above argument will only apply provided that the stationary phases themselves are capable of efficiently resolving mixtures. Table I shows the number of theoretical plates required for unit resolution (98% separation) of a series of two-component mixtures at 180° and a flow-rate of 20 ml/min. The HETP values obtained using *n*-butylbenzene are included for comparison. Apiezon L shows superior resolving power for only one class of compounds, the paraffins. For aromatic hydrocarbon separation, Apiezon L and polybenzyl are comparable but on introduction of almost any type of functional group into sample components, polybenzyl becomes a far superior stationary phase to Apiezon L. This effect is more apparent in the separation of esters or alcohols, where polybenzyl must be the preferred stationary phase.

At 180° polystyrene is not being used under optimum conditions. However, even at this temperature, it proves to be a superior stationary phase to Apiezon L for the separation of carbonyl and nitro compounds and alcohols. In fact, polystyrene

is so superior for nitro compounds and alcohols that the effect of plasticizing with Apiezon L in order to decrease the viscosity is more than offset by the incorporation of the inferior stationary phase so that the polystyrene phase is more effective than its plasticized counterpart.

Table II lists the retention indices ( $I$ ) determined on the stationary phases for several aromatic compounds. The use of the Rohrschneider<sup>9</sup> solutes for determination of column polarity is not possible at the high column temperatures used here but, in order to give some comparison with the accepted method of assessment of column polarities in this and future work on high-temperature phases, the aromatic analogues of the Rohrschneider solutes were chosen *i.e.* aromatic hydrocarbon, ketone, nitro compound, alcohol and nitrogen base. It is tentatively suggested that at 180° solutes 1–5 in Table II form the basis of a complementary method to the Rohrschneider

TABLE I  
NUMBER OF THEORETICAL PLATES REQUIRED FOR UNIT RESOLUTION OF TWO-COMPONENT MIXTURES

Mixtures	$n_{req.}$			
	Apiezon L	Polystyrene	Polystyrene + Apiezon L	Polybenzyl
<i>n</i> -Decane– <i>n</i> -dodecane	69	111	94	87
Mesitylene– <i>n</i> -butylbenzene	343	456	394	335
Benzaldehyde– acetophenone	210	162	149	230
Methyl benzoate– isoamyl butyrate	125	66	64	55
Nitrobenzene– <i>p</i> -nitrotoluene	100	81	100	81
Benzyl alcohol– cyclohexanol	125	58	89	59
HETP ( <i>n</i> -butylbenzene)	0.34	1.0	0.64	0.22

TABLE II  
RETENTION INDICES ( $I$ ), AT 180°, OF AROMATIC COMPOUNDS ON HYDROCARBON STATIONARY PHASES

Solute	$I$		
	Apiezon L	Polystyrene	Polybenzyl
1 <i>n</i> -butylbenzene	1108	1245	1224
2 acetophenone	1130	1414	1381
3 nitrobenzene	1168	1467	1436
4 benzyl alcohol	1097	1422	1359
5 aniline	1048	1348	1289
6 methyl benzoate	1140	1412	1366

classification system<sup>9</sup> for the evaluation of high-temperature stationary phases.

Although all the phases discussed in this paper are effectively non-polar, Table II provides an interesting comparison. Polystyrene as a stationary phase leads to a retention increment ( $\Delta I$ ) over Apiezon L of about 300 whilst the polybenzyl increment is about 250. The explanation offered for this higher retention on polystyrene concerns the structure of the two hydrocarbons. Increased retention over Apiezon L must be by induced dipole effects involving the  $\pi$  electrons of the aromatic rings. In the *para*-linked polybenzyl, the rings are part of the molecular chain, however in polystyrene, the chain is an aliphatic hydrocarbon structure containing pendant phenyl groups. The pendant phenyl will be the more accessible to an incoming solute molecule hence solute-solvent interaction will be favoured in polystyrene over polybenzyl. From Table II, this stationary phase steric factor would appear to be responsible for a  $\Delta I$  of about 50 units.

In conclusion, the results given here have been vindicated by the separations of many mixtures on the four columns at various temperatures. One example is the attempted separation of phenol and the three cresol isomers at 180°. Apiezon L gave a chromatogram in which phenol was partially separated from the cresol peak whilst the polybenzyl phase gave complete resolution of phenol with partial separation of *o*-cresol (b.p. 190°) from the *m+p* cresol peak (these two isomers differ by only 1° in b.p.). Another example is the separation of *n*-butylbenzene (b.p. 180°), acetophenone (202°) and nitrobenzene (210°). At 180°, Apiezon L gave partial resolution of *n*-butylbenzene but no separation of acetophenone and nitrobenzene.

Plasticized polystyrene gave 98% resolution ( $R=1$ ) of *n*-butylbenzene with partial resolution of the acetophenone-nitrobenzene peak. Polybenzyl gave complete resolution of *n*-butylbenzene with good resolution of the acetophenone-nitrobenzene peak ( $R=0.87$ ).

Polybenzyl is a more efficient stationary phase than Apiezon L at lower temperatures, up to its maximum at 240°. In the region 240-340°, a linear polystyrene stationary phase is preferred.

## REFERENCES

- 1 Shell Chemicals, *Tech. Bull.*, 1CS(X)/70/20.
- 2 W. Gerrard, S. J. Hawkes and E. F. Mooney, in R. P. W. Scott (Editor), *Gas Chromatography*, Butterworths, London, 1960.
- 3 O. L. Hollis, *Anal. Chem.*, 38 (1966) 309.
- 4 K. I. Sakodynski and L. I. Panina, *J. Chromatogr.*, 58 (1971) 61.
- 5 J. J. van Deemter, F. J. Zuiderweg and A. Klinkenberg, *Chem. Eng. Sci.*, 5 (1956) 271.
- 6 J. H. Purnell, *Nature (London)*, 184 (1959) 2009.
- 7 J. H. Purnell, *J. Chem. Soc., London*, (1960) 1268.
- 8 E. Kováts, *Helv. Chim. Acta*, 41 (1958) 1915.
- 9 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.