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## POLARITY OF POLYESTER STATIONARY PHASES

F. VERNON

*Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT Lancashire (Great Britain)*

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### SUMMARY

Sets of polyester condensates have been compared as stationary phases in gas-liquid chromatography by determination of their polarity constants both from the Rohrschneider probes at low temperature and using a set of aromatic probes at high temperature. It was found that isomeric polyesters do not have the same polarities and, from the concept of methylene transfer between the diol and acid backbones of the polymers, a general conclusion is reached that transfer of methylene groups from the diol to the acid backbone increases the polarity of the phase. The lower (more polar) members of the series, however, displayed anomalous behaviour. An examination of poly(methyl methacrylate) as a possible high-temperature polyester phase was carried out. This addition polymer displayed a lower polarity than its isomeric polycondensates and, although stable to a working temperature of 280°, the material proved unsatisfactory in performance—low column efficiencies were observed as a result of the high viscosity of the material.

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### INTRODUCTION

In the search for stationary phases that are stable at high temperatures, the properties of polystyrene<sup>1</sup> and of polyethylene<sup>2</sup> have been studied. For a high-temperature phase of a more polar nature, a polyester, poly(methyl methacrylate) would seem to be an obvious choice. Its high-temperature stability and performance as a stationary phase have therefore been evaluated. For comparison, two condensation polyesters that are isomeric with poly(methyl methacrylate), namely poly(butanediol adipate) and poly(ethanediol suberate), were included in the study. The vinyl polymer is so different in structure, with its pendant carboxymethoxy groups, from the two polycondensates where the ester function is "in-chain" that different polarities could be expected. However, significant variations in retention indices, indicating different polarities, were found for the two polycondensates. As the difference between these two isomers only involves the transfer of methylene groups from the diol chain to the diacid chain and vice versa, it would seem that this transfer changes the polarity, therefore the two types of methylene groups present are not equivalent. To explore this fully, a wide range of polyester condensates were synthesized (a) where the number

of methylene groups in the diol chain was held constant, *i.e.* a set of poly(butanediol) esters, and (b) where the number of methylenes in the dibasic acid part of the molecule was constant, *i.e.* a set of polydiol adipates. The behaviour of these polyester phases and the effect on polarity of transfer of a methylene group is described here in terms of retention indices and Rohrschneider constants<sup>3</sup> for the phases, and also in terms of modified column constants derived by the use of aromatic probes at a temperature of 180°. These probes for high-temperature evaluation have been described in earlier work<sup>1,2</sup> and were necessary for the evaluation of the poly(methyl methacrylate) phase whose glass-to-rubber transition temperature is in the region of 120°.

## EXPERIMENTAL

The instrument used in this work was a Pye Series 104 gas chromatograph with flame ionization detector. All columns were 1 m × 6 mm O.D. copper tubing, packed with a 10% (w/w) coating of stationary phase on Chromosorb W AW DCMS, they were conditioned at 180° and a flow-rate of 10 ml/min of nitrogen for 24 h. All measurements were made using a carrier gas flow-rate of 20 ml/min, the evaluation using Rohrschneider solutes being carried out at a temperature of 100° and the work using the aromatic probes *n*-butylbenzene, benzyl alcohol, acetophenone, nitrobenzene and aniline being carried out at 180°.

### *Stationary phases*

Laboratory reagent grade diols and dibasic acids were further purified by crystallisation, vacuum distillation or zone refining as appropriate. Polyester condensates were prepared by mixing exactly equimolar quantities of a diol and a dibasic acid and heating at 140° for 12 h, thereby minimizing end-group effects. Poly(methyl methacrylate), obtained in the form of Perspex sheet, was purified by dissolving in chloroform and precipitating the polymer by the addition of methanol. The polyester condensates prepared were: (a) polyester adipates of ethanediol, butanediol, hexanediol and decanediol; (b) poly(butanediol) esters of succinic, adipic, suberic and dodecanedioic acids. Poly(ethanediol suberate) was also prepared, squalane (100°) and Apiezon L (180°) were used as non-polar reference phases.

Column dead-times were determined by injection of methane. Retention indices of the solutes were obtained by chromatographing with the two appropriate *n*-paraffins and using the Kováts formula<sup>4</sup>.

Thermogravimetric measurement on the poly(methyl methacrylate) column packing was carried out on a thermal balance with the sample in a nitrogen atmosphere, flow-rate 10.0 ml/min. Rate of temperature increase 2°/min.

Column efficiency and HETP value as a function of temperature were obtained at a constant flow-rate of nitrogen of 20 ml.min using six aromatic hydrocarbons each being used to determine the efficiency at a column temperature corresponding to its boiling point. The six hydrocarbons and temperatures were toluene (110°), *p*-xylene (137°), propylbenzene (158°), *n*-butylbenzene (180°), naphthalene (218°) and diphenylmethane (261°). Three of the polyester stationary phases were examined for their ability to separate pairs of structurally similar compounds. These pairs were (i) 2-butanone and *n*-butyraldehyde, chosen because they are isomeric, their boiling points are similar, and the compound with the lower boiling point (*n*-butyraldehyde) is the

more polar as determined by dipole moment, (ii) methyl propionate and methyl acrylate, chosen as a closely related pair of esters differing only in that the latter possesses a double bond.

## RESULTS AND DISCUSSION

Thermogravimetry of the poly(methyl methacrylate) coated column packing revealed that the stationary phase is stable to 290°, above which temperature rapid degradation occurs due to the unzipping of the polymer chains. HETP values determined using the six aromatic hydrocarbons at their boiling points were; 6.5 cm (158°), 2.9 cm (180°), 1.0 cm (218°) and 0.7 cm (261°). Taking the lower temperature limit as that at which HETP is 1 cm and the upper limit at 10° below degradation, gives a working range of 220–280° for this stationary phase. Using a column temperature of 250°, attempts were made to separate some glycerol triesters on this phase as their boiling points and retention indices on poly(methyl methacrylate) suggested that separation should be possible. The data obtained for retention indices at 250° (with boiling points in brackets) were glycerol triacetate 1595 (258°), glycerol tripropionate 1811 (289°) and glycerol tributyrates 1929 (318°). The polymer would not separate the three triesters, furthermore when a mixture of glycerol triacetate and tributyrates was chromatographed, the resolution obtained was a mere 0.54. The polymer was not considered to be suitable stationary phase material for high-temperature work and further separations on the phase were not attempted.

The retention indices of the aromatic probes had been determined at 180° on poly(methyl methacrylate) and the values, together with values of the isomeric polyesters poly(butanediol adipate) and poly(ethanediol suberate), are given in Table I. It is apparent from the values given, that poly(methyl methacrylate) is considerably less polar than poly(ethanediol suberate) or poly(butanediol adipate) with the latter isomer being slightly the more polar of the two. In Table I, where all the polyesters are grouped in isomeric pairs and the total number of methylene groups present in the

TABLE I  
RETENTION INDICES OF AROMATIC COMPOUNDS ON POLYESTER STATIONARY PHASES (at 180°)

Stationary phase	$I_{180^\circ}$				
	<i>n</i> -Butylbenzene	Benzylalcohol	Acetophenone	Nitrobenzene	Aniline
Poly (ethanediol adipate)	1366	1873	1867	1823	1758
Poly (butanediol succinate)	1404	1884	1892	1852	1206
Poly (butanediol adipate)	1317	1748	1765	1707	1648
Poly (ethanediol suberate)	1305	1755	1756	1681	1638
Poly (methyl methacrylate)	1241	1683	1684	1661	1588
Poly (hexanediol adipate)	1274	1627	1630	1600	1539
Poly (butanediol suberate)	1281	1635	1635	1602	1533
Poly (decanediol adipate)	1228	1471	1472	1463	1383
Poly (butanediol dodecanedioate)	1238	1492	1495	1486	1398
Apiezon L	1108	1017	1130	1168	1048

monomer unit increases on going down the table, two points are obvious. First, as the total methylenes increase there is a decrease in retention index, and secondly that there is no agreement nor even an apparent trend in the behaviour of the retention indices within isomeric groups.

Using a Rohrschneider type of equation<sup>5</sup>, with Apiezon L as the reference phase for  $\Delta I$  calculation,

$$\Delta I = ax + by + cz + du + es$$

and making  $a = 100$  for butylbenzene,  $b = 100$  for benzyl alcohol,  $c = 100$  for acetophenone,  $d = 100$  for nitrobenzene and  $e = 100$  for aniline (all other constants for each probe being zero), enables the calculation of a series of stationary phase (or column) constants for the polyesters. These values are shown in Table II. It can be seen from this table that methylene groups in the diol backbone and the dibasic acid backbone are not equivalent even when the paraffin chains are very long. Table III gives the retention indices found for the Rohrschneider solutes and Table IV gives the corresponding stationary phase constants. Comparison of the values in Tables II and IV leaves no doubt about the methylene non-equivalence hypothesis. Table IV, with the exception of the pyridine results which seem to be anomalous, confirms the findings at the higher temperature. Some anomalies are present, and in Figs. 1a-e, are plotted the five column constants obtained for each phase at each temperature, the column constants for the series of adipates and butanediol polyesters being plotted against number of methylene groups in the variable part of the polyester molecule. The trends now become apparent, the main conclusion being that, for an isomeric pair of polyesters, transfer of methylene groups from the diol backbone to the acid backbone increases the polarity of the phase. The first pair in the series, poly(ethanediol adipate) and poly(butanediol succinate) display unusual behaviour but this is to be expected when the number of methylene groups between functional units is as low

TABLE II  
COLUMN CONSTANTS (DERIVED FROM THE AROMATIC SOLUTES) FOR THE POLYESTERS

Stationary phase	$x_{ar}$	$y_{ar}$	$z_{ar}$	$u_{ar}$	$s_{ar}$
Poly (ethanediol adipate)	2.58	7.76	7.37	6.55	7.10
Poly (butanediol succinate)	2.96	7.87	7.62	6.24	7.58
Poly (butanediol adipate)	2.09	6.51	6.35	5.35	6.00
Poly (hexanediol adipate)	1.66	5.30	5.05	4.32	4.11
Poly (butanediol suberate)	1.73	5.38	5.05	4.34	4.80
Poly (decanediol adipate)	1.20	3.74	3.42	2.95	3.30
Poly (butanediol dodecanedioate)	1.30	3.95	3.65	3.18	3.50
Poly (ethanediol suberate)	1.17	6.58	6.26	5.13	5.90
Poly (methyl methacrylate)	1.33	5.86	5.04	4.93	5.40
Apiezon L (reference)	0	0	0	0	0

TABLE III

RETENTION INDICES OF ROHRSCHEIDER SOLUTES ON POLYESTER STATIONARY PHASES (at 100°)

<i>Stationary phase</i>	$I_{100}^{\circ}$				
	<i>Benzene</i>	<i>Ethanol</i>	<i>2-Butanone</i>	<i>Nitromethane</i>	<i>Pyridine</i>
Poly (ethanediol adipate)	930	867	901	1098	1198
Poly (butanediol succinate)	931	853	898	1110	1201
Poly (butanediol adipate)	894	802	849	1020	1134
Poly (hexanediol adipate)	849	745	800	947	1089
Poly (butanediol suberate)	858	746	805	948	1070
Poly (decanediol adipate)	799	663	741	837	1030
Poly (butanediol dodecanedioate)	808	685	745	841	997
Squalane	649	384	531	457	695

TABLE IV

COLUMN CONSTANTS FOR THE POLYESTERS

<i>Stationary phase</i>	<i>x</i>	<i>y</i>	<i>z</i>	<i>u</i>	<i>s</i>
Poly (ethanediol adipate)	2.21	4.83	3.70	6.41	5.03
Poly (butanediol succinate)	2.82	4.69	3.67	6.53	4.10
Poly (butanediol adipate)	2.45	4.18	3.18	5.63	4.41
Poly (hexanediol adipate)	2.00	3.61	2.69	4.90	3.87
Poly (butanediol suberate)	2.09	3.62	2.74	4.91	3.79
Poly (decanediol adipate)	1.50	2.79	2.10	3.80	3.35
Poly (butanediol dodecandioate)	1.59	3.01	2.14	3.84	3.02

as two. Thus, from Rohrschneider probe data, it can be seen that the *x* values are the same, the *y* and *z* values both giving poly(ethanediol adipate) as the more polar phase. Of the high temperature probes, agreement is complete, demonstrating that above a minimum chain length, polarity increases on methylene transfer from diol to acid. The isomeric pair chosen for comparison with poly(methyl methacrylate) have been studied only by the high temperature system and, as the diol chain in poly(ethanediol suberate) contains only two methylene groups, give anomalous results.

The two most polar polyesters, poly(butanediol succinate) and poly(ethanediol adipate), together with one of the least polar phases, poly(decanediol adipate), were chosen for examination. Two pairs of similar solutes were chromatographed on these phases, the first pair being 2-butanone (b.p. 80°) and *n*-butyraldehyde (b.p. 74°), of which the latter has the higher dipole moment. The second pair were methyl propionate (b.p. 79°) and methyl acrylate (b.p. 85°). The column temperature in each case being 80°. Table V gives the retention indices of the solutes on each of the stationary phases, the ketone-aldehyde values being particularly interesting. The polyester of low polarity separates these two substances in order of boiling points. Of the two polar phases it has been established from Table II that poly(ethanediol adipate) is the less

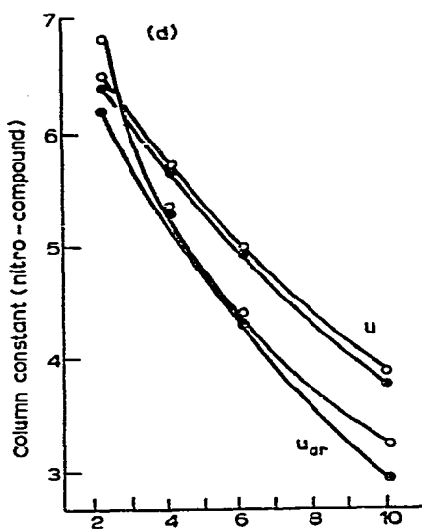
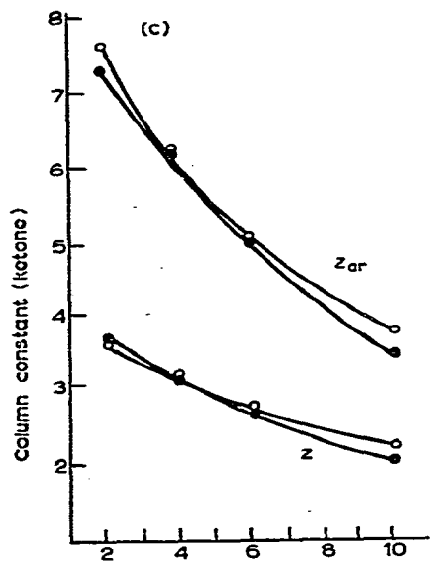
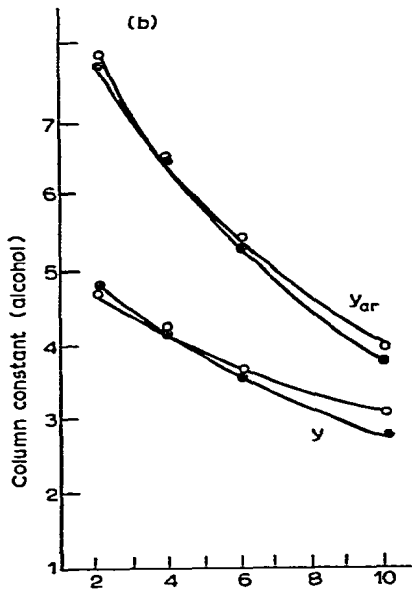
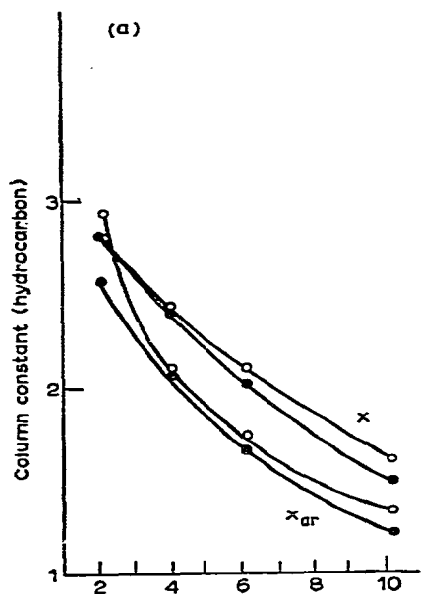


Fig. 1.

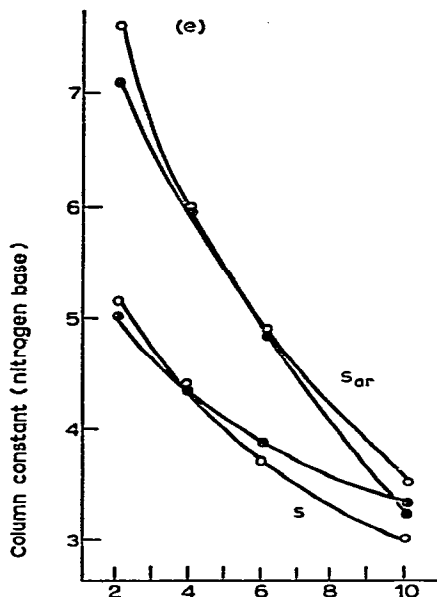


Fig. 1. Plots of the variation of Rohrschneider constants ( $x$ ,  $y$ ,  $z$ ,  $u$  and  $s$ ) (a to e, respectively) and column constants derived from the aromatic solutes ( $x_{ar}$ ,  $y_{ar}$ ,  $z_{ar}$ ,  $u_{ar}$  and  $s_{ar}$ ) against number of methylene groups in the diol chain of adipate polyesters (●) and in the acid chain of butanediol polyesters (○).

TABLE V

RETENTION INDEX VALUE OF SOME SOLUTES ON SELECTED POLYESTER PHASES AT 80°

Stationary phase	2-Butanone	<i>n</i> -Butyraldehyde	Methylpropionate	Methylacrylate
Poly (butanediol succinate)	866	877	869	895
Poly (ethanediol adipate)	910	888	906	930
Poly (decanediol adipate)	737	729	742	750

polar whereas the data in Table IV suggests that it is the more polar. On this phase, butyraldehyde has a lower retention index than the ketone, consequently the elution is in order of boiling point. On the succinate, the reverse is found with selective retention of the more polar aldehyde, the ketone being eluted first. For the ester pair, whereas the decanediol ester has low polarity and tends to separate on boiling points with a difference between the esters ( $\Delta I$ ) of 8 units, differences between the esters on the polar phases are 26 and 24 units—the slightly larger value found, as expected, on the slightly more polar succinate phase.

Using the four diols and dibasic acids used here, it is possible to generate a set of sixteen polyester stationary phases with a wide range in polarity from the highly polar poly(ethanediol succinate) to the virtually non-polar poly(decanediol dodecanedioate) each with its own set of polarity values. Selection of the optimum phase from amongst these sixteen should enable good separations of complex mixtures to be

achieved, for instance in the field of vegetable oil analysis where separations of methyl esters of the fatty acids are complicated by the presence of mono- and diunsaturated esters.

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