CHROM. 10,463

POROUS POLYAROMATIC BEADS

II*. THE USE OF BROMINATED POLYMERS IN GAS CHROMATOGRAPHY

JOHN R. LINDSAY SMITH, ADNAN H. H. TAMEESH** and DAVID J. WADDINGTON***

Department of Chemistry, University of York, York YO1 5DD (Great Britain)

SUMMARY

Two commercially available porous aromatic polymer beads used for gas chromatography, Porapak Q and Chromosorb 102, have been brominated. The resulting polymers are significantly more stable to heat and, when treated with bromine in tetrachloromethane (with or without thallium(III) acetate), the materials become much more suitable for the separation of polar adsorbates such as alcohols and carboxylic acids. The retention times of the adsorbates depend on the method of bromination used.

INTRODUCTION

Following their introduction by Hollis[1] and Hollis and Hayes[2] porous aromatic polymers have now been used in gas chromatography (GC) for some ten years[3,4].

Recently we have synthesized a range of porous polymers, using 4-substituted styrenes as monomers and divinylbenzene as the cross-linking agent, in order to elucidate their mode of action in GC[5,6]. In the course of the study, we were concerned with the effect of the unreacted vinyl groups in the polymers, and, in investigating this aspect, brominated some porous polymer beads using a variety of methods. The chromatographic characteristics of the polymers changed considerably on chemical treatment and some of the resulting materials have distinct advantages over untreated packing materials. This paper is concerned with the commercial polymers following bromination and concentrates on their advantages in GC, particularly for the analysis of polar compounds and for work at temperatures above 250°, conditions under which Porapak Q and Chromosorb 102 tend to deteriorate.

---

* For Part I see ref. 5.
** Present address: Iraq Petroleum Research Institute, Council of Scientific Research, Baghdad, Iraq.
*** To whom correspondence should be addressed.

TABLE I

PROPERTIES OF SOME POROUS POLYAROMATIC BEADS

HETP values were obtained at 140° with pentane as adsorbate and carrier gas (nitrogen) at 50 ml/min. ND = not determined.

Polymer	Treatment	Code	Analysis (% w/w)			HETP (mm)	Enthalpies of adsorption (kJ/mol) *		Approximate endothermal degradation temperature (°C)**
			C	H	Br		Pentane	Ethanol	
Porapak Q	—	PQ	90.82	8.29	—	3.2	45.0	ND	240
Chromosorb 102	—	C-102	91.98	8.03	—	ND	46.9	ND	240
Porapak Q	Bromine–tetrachloromethane–thallium(III) acetate	PQ/Br(Tl)	74.83	6.85	18.6	3.7	47.4	ND	450
Chromosorb 102	Bromine–tetrachloromethane	C-102/Br	79.93	7.21	12.8	ND	49.7	40.9	ND
Chromosorb 102	Bromine–tetrachloromethane–thallium(III) acetate	C-102/Br(Tl)	68.82	6.01	24.3	ND	47.2	ND	430
Chromosorb 102	Bromine–water	C-102/Br(H_2O)	78.01	6.83	ND	ND	45.9	43.3	ND

* Error to within ±0.7 kJ/mol. Four determinations of t'_r between 85° and 200°.

** As determined by differential thermal analysis.

EXPERIMENTAL

Preparation of the brominated polymers

Two commercial porous polyaromatic beads, Porapak Q (Waters Assoc., Milford, Mass., U.S.A.) and Chromosorb 102 (Johns-Manville, Denver, Colo., U.S.A.) were brominated. In all, three different methods were used. In one method, the polymer beads were suspended in tetrachloromethane and gently stirred. A solution of bromine in the organic solvent was added until the colour of bromine persisted. The solution was warmed to about 50° for about 2 h. The beads were recovered by filtration, washed in tetrachloromethane and subsequently with acetone. Finally, they were dried under vacuum at 80° for 8 h. A similar procedure was adopted for the other two methods of bromination. In one, the same solvent was used but thallium(III) acetate sesquihydrate (Aldrich, Gillingham, Great Britain) was dissolved in the solution of bromine[7,8]. In the other, the polymer beads were suspended in water, and a saturated solution of bromine in water was added.

Elemental analyses of the polymers (carbon, hydrogen) were done on a Perkin-Elmer CHN elemental analyser. Other elements were determined by the Butterworth Microanalytical Consultancy (Teddington, Great Britain).

Infrared (IR) analyses of the polymers were performed on a Perkin-Elmer 621 spectrophotometer (range 200–4000 cm^{-1}) using potassium bromide discs and pellets for liquid and solid samples, respectively.

Thermal analyses of polymers were made on a DuPont 900 differential thermal analyser, with glass beads as a reference. The polymers were heated at a rate of 20°/min under an atmosphere of nitrogen.

Chromatography

All GC results were determined on Pye Series 104 chromatographs, equipped with dual flame ionization or thermal conductivity detectors.

Columns were of Pyrex glass and ranged in length from 0.45 to 1.5 m with an I.D. of 4 mm. Injections of liquids and solutions were made by dipping the tip of a microlitre syringe into the sample and immediately injecting the sample without altering the plunger position from zero. Only the sample entrapped in the capillary between the barrel and plunger was injected and consistent values for the retention volumes were obtained[5].

Height equivalent to a theoretical plate (HETP) values were measured at 140°, with a nitrogen flow-rate of 50 ml/min and pentane as adsorbate.

Isosteric enthalpies of adsorption were obtained by measuring retention volumes at at least four temperatures between 85° and 200°.

RESULTS AND DISCUSSION

Details of the elemental composition of the polymers are given in Table I. As expected, the extent of bromination depends on the reaction conditions. Thus, when thallium(III) acetate is present in the reactant mixture, the extent of bromination is increased. Thallium(III) catalyses substitution on the phenyl ring, and this process occurs as well as the normal addition reaction to the vinyl groups[7]. Bromination did not greatly affect the HETP value of the polymer (Table I).

TABLE II

ADJUSTED RETENTION TIMES, RELATIVE TO PENTANE, FOR ADSORBATES ON SOME POROUS POLYMERS

Carrier gas, nitrogen at 50 ml/min. Polymers, see Table I. Temperature, 151°. ND = not determined.

Adsorbate	Polymer					
	PQ	PQ/Br(Tl)	C-102	C-102/Br	C-102/Br(Tl)	C-102/Br(H₂O)
Pentane	1.00 (54.2)*	1.00 (54.3)	1.00 (26.3)	1.00 (22.1)	1.00 (31.5)	1.00 (17.5)
Hexane	2.51	2.68	2.29	2.36	2.50	2.23
1-Hexene	2.15	2.31	2.03	2.10	2.30	2.09
Methanol	0.16	0.13	0.23	0.21	0.16	0.25
Ethanol	0.36	0.34	0.43	0.41	0.40	0.52
1-Propan-1-ol	0.95	0.93	1.03	1.15	1.09	1.24
1-Butan-1-ol	2.54	2.59	2.57	3.05	2.87	3.18
1-Pentan-1-ol	ND	ND	7.10	—	8.00	—
Formic acid	0.36	0.25	0.41	0.35	0.29	0.45
Acetic acid	0.86	0.73	0.98	1.00	0.86	1.09
Propionic acid	2.25	1.98	2.31	2.46	2.18	2.68
2-Methylpropionic acid	4.67	4.29	4.50	4.68	4.48	5.07
Dichloromethane	0.70	0.68	0.86	0.83	0.80	0.86
Trichloromethane	1.65	1.63	1.79	2.09	1.78	1.94
Tetrachloromethane	2.77	2.83	2.93	3.05	3.04	2.91
1,2-Dichloroethane	2.10	2.13	2.99	2.50	2.41	2.53
1-Bromo-2-methylpropane	4.32	4.45	4.25	4.58	4.69	4.47
2-Bromobutane	4.14	4.41	4.14	4.52	4.67	4.41
Propane-1,2-diol	ND	ND	4.18	4.62	4.09	6.51
Benzene	2.77	2.90	3.07	ND	3.14	ND
Toluene	6.26	6.54	7.52	ND	7.86	ND
Ethylbenzene	15.13	16.41	16.65	ND	18.21	ND
1,2-Dimethylbenzene	18.88	19.45	20.41	ND	22.57	ND
1,3-Dimethylbenzene	16.36	17.41	18.30	ND	20.88	ND
1,4-Dimethylbenzene	16.88	17.06	14.83	ND	19.62	ND
Nitromethane	ND	ND	1.03	ND	1.00	ND
Nitroethane	ND	ND	2.21	ND	2.26	ND
1-Nitropropane	ND	ND	4.86	ND	5.21	ND
1-Nitrobutane	ND	ND	8.76	ND	9.79	ND

* Values in parentheses represent specific retention volumes (ml/g).

The thermal stability of a stationary phase is of fundamental importance for GC analysis, particularly of compounds of high relative molecular mass.

It has been reported many times that the Porapak and Chromosorb 100 series of polymers tend to deteriorate above *ca.* 250° and we found that our samples of Porapak Q and Chromosorb 102 degraded at *ca.* 240°. Yet this is somewhat lower than the reported degradation temperatures of styrene–divinylbenzene co-polymers which are above 300°[9,10], and substitution of ethylvinylbenzene for styrene is unlikely to alter this temperature markedly: alkyl substitution on the benzene ring has little effect on the endothermal degradation temperatures[11,12].

In contrast, following bromination of these two commercial polymers, their decomposition temperatures as measured by differential thermal analysis are raised to *ca.* 430° (Table I). Presumably, under nitrogen, depolymerization occurs at elevated temperatures and bromination of the free vinyl groups reduces this tendency. A similar although less marked effect, was noted on treating Chromosorb 102 with performic and formic acids to produce the formate ester, the decomposition temperature being raised from 220° to 275°.[13] Similarly, when the ester groups were hydrolysed to form hydroxyl groups, the decomposition temperature was further raised to 290°[13].

Analyses of some polar materials are difficult to achieve on commercial porous aromatic polymers, and this has been ascribed to the presence of unreacted vinyl groups in the polymer[14,] present from partially reacted divinylbenzene. Indeed both commercial polymers show clearly, on analysis by IR spectroscopy, the presence of these groups. There are strong absorptions at 3080 and 3046 cm^{-1}, corresponding to =C–H stretching and at 985 and 900 cm^{-1}, corresponding to =C–H deformation. These absorptions, following bromination, decrease by 60 $\pm$ 5%, as measured by a base-line method[15].

There is a corresponding appearance of bands attributable to C–Br (590 cm^{-1}) and, when thallium(III) acetate is present in the reaction mixture, of bands at 1070 and 1008 cm^{-1}, characteristic of 4-bromo-1-substituted benzenes. When the polymers have been treated with bromine water, absorptions are seen at 3590–3570 cm^{-1}, characteristic of –OH groups.

There is a great improvement in the separation of polar compounds on porous polymers following bromination. This suggests that although not all the vinyl groups have been removed, they are in the bulk of the polymer which neither the bromine solutions nor the adsorbates can reach.

Analyses of some polar materials which are difficult to achieve on porous aromatic polymers have been facilitated by coating the polymer with a liquid[16–19]. Thus, one could envisage that the commercial polymers, following bromination, could be used likewise, with liquid phases such as the carborane silicones or the phenyl and alkyl silicones themselves, which are stable to *ca.* 400°, thus increasing considerably the temperature range for this valuable technique.

There are distinct differences in relative retention times for compounds on brominated polymers, depending on the brominating agent used (Table II). In a subsequent paper[6], the mode of action of porous aromatic polymers in GC is discussed in detail. However, the results in Table II are of intrinsic interest in themselves. One can regard the interactions between adsorbate and adsorbent in terms of intermolecular forces due to dipole and induced-dipole interactions.

Bromination of the commercial polymers by the three methods leads to (a)

TABLE III

RETENTION INDEX DIFFERENCES (I.U.) OF BENZENE (x) 1-BUTANOL (y) AND 2-PENTANONE (z) ON SOME POROUS POLYMERS, USING GTCB AS REFERENCE, AND THE GENERAL SELECTIVITY INDEX (ΣI) FOR THE POLYMERS AT 140° (REF. 22)

Polymers, see Table I.

Polymer	x	y	z	ΣI^*
PQ	43	118	86	247
C-102	48	119	88	255
C-102/Br	49	129	102	280
C-102/Br (Tl)	41	127	109	277
C-102/Br (H₂O)	56	146	123	325

* Errors are within $\pm$ 3 I.U.

bromination of the vinyl groups, (b) bromination of the vinyl groups and the phenyl rings, (c) bromination and hydroxylation of the vinyl groups. The effect of the last, that of adding a polar hydroxyl group to Chromosorb 102, is to increase the relative retention times for the alcohols and acids, and to leave, relatively unaffected, the relative retention times of compounds with small or zero dipole moments such as the alkanes and the halogenoalkanes. However, the effect of simply brominating the vinyl groups is to reduce, relative to that of non-polar compounds, the relative retention times of the polar compounds, presumably because the loss of the vinyl group interactions is not compensated for by interactions due to the presence of the large polarizable bromine atoms. Finally bromination, with thallium(III) present, increases this effect. Relative to the original polymer, the characteristics that enhance non-polar interactions (dispersion forces) have increased further the relative retention times for the non-polar adsorbates, but have decreased the polar characteristics of the polymer. Similar trends can be seen on examining the enthalpies of adsorption for a non-polar (e.g. pentane) and a polar (e.g. ethanol) adsorbate on the polymers (Table I).

Another way of expressing the change in the polymers on bromination is shown in Table III. In this method, which is discussed in a further paper[6], the retention indices of three of McReynolds'[20], standard substances (benzene, 1-butanol and 2-pentanone) are determined using retention indices on graphitized thermal carbon black (GTCB) for these substances as reference[21].

Bromination of porous aromatic polymers leads, therefore, to a greater thermal stability, a reduction of tailing of polar adsorbates, and the ability to alter relative retention times of many adsorbates, thus increasing the usefulness of these important stationary phases.

REFERENCES

1 O. L. Hollis, *Anal. Chem.*, 38 (1966) 309.
2 O. L. Hollis and W. V. Hayes, *J. Gas Chromatogr.*, 4 (1966) 235.

3 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
4 O. L. Hollis, *J. Chromatogr. Sci.*, 11 (1973) 335.
5 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 148 (1978) 353.
6 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, in press.
7 A. McKillop, D. Bromley and E. G. Taylor, *Tetrahedron Lett.*, 21 (1969) 1623.
8 F. Camps, J. Castells, M. J. Ferrando and J. Font, *Tetrahedron Lett.*, (1971) 1713.
9 C. H. Winslow and W. Matreyek, *J. Polym. Sci.*, 23 (1956) 315.
10 S. Straus and S. L. Madorsky, *J. Res.*, *NBS*, 65A (1961) 243.
11 F. Danusso and G. Polizzotti, *Makromol. Chem.*, 61 (1963), 157.
12 L. Reich, *Macromol. Rev.*, 3 (1968) 49.
13 R. A. Gilhooley and P. A. Sewell, unpublished results.
14 W. Hertl and M. G. Neumann, *J. Chromatogr.*, 60 (1971) 319.
15 W. Brugel, *An Introduction to Infrared Spectroscopy*, Wiley, New York, 1962, p. 300.
16 J. R. Lindsay Smith and D. J. Waddington, *Anal. Chem.*, 40 (1968) 522.
17 J. R. Lindsay Smith and D. J. Waddington, *J. Chromatogr.* 36 (1968) 145.
18 B. O. Jansson, R. Hallgren and R. Widmark, *J. Chromatogr.*, *Sci.*, 8 (1970) 398.
19 W. Johnson, R. W. Hale and J. W. Nedlock, *Tobacco*, 175 (1973) 32.
20 W. O. McReynolds, *J. Chromatogr. Sci.*, 8 (1970) 685.
21 E. V. Kalashnikova, A. V. Kiselev, D. P. Poshkus and K. D. Shcherbakova, *J. Chromatogr.*, 119 (1976) 233.
22 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, in press.