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POROUS POLYAROMATIC BEADS

I. THE PREPARATION, CHARACTERIZATION AND USE IN GAS CHROMATOGRAPHY OF CHEMICALLY MODIFIED POROUS POLYAROMATIC BEADS

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SUMMARY

A selection of chemically modified porous polyaromatic beads for gas chromatography has been prepared either by polymerization of a substituted styrene and divinylbenzene or by chemical derivatization of polymers prepared from divinylbenzene and styrene or ethylvinylbenzene. The chemical composition and hence the extent of chemical modification of the polymers was examined by elemental analysis and infrared spectroscopy. The physical characteristics of the beads were examined by electron microscopy and differential thermal analysis.

The chromatographic behaviour of a wide range of organic compounds on the polymers was studied. Almost all the compounds gave symmetrical peaks on the adsorbates. However, carboxylic acids and some alcohols showed peak tailing on some of the columns. The effect of chemical modification on the adjusted retention times of the compounds is discussed.

INTRODUCTION

Porous polyaromatic beads have been used extensively in gas chromatography (GC), since their introduction by Hollis¹ and Hollis and Hayes², for the separation of a wide range of compounds (see *e.g.*, refs. 3 and 4). To extend the range of uses of these polyaromatic beads and to change their chromatographic behaviour they have been modified by surface coating⁵⁻⁹. However, the possibility of producing a range of solid phases by chemical derivatization of the porous polymers has received relatively little attention^{10,11}. By contrast, in organic synthesis, chemically modified styrene-divinylbenzene (DVB) polymers have been prepared and used with great success for making insoluble polymer bound organic reagents^{12,13}.

Interest in the effect of chemical modification on the chromatographic properties of porous polyaromatic beads and in the molecular interactions that are involved

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in GC has led us to prepare a selection of closely related derivatized porous polyaromatic beads. These have been prepared by either polymerization of substituted styrenes and DVB (polymers I) or by chemical modification of polymers prepared from DVB and styrene or ethylvinylbenzene (EVB) (polymers II).

In this paper, the preparation and properties of these phases are described. In following papers we use these phases to develop a method for classifying the polarities of solid phases in GC¹⁴ and we examine the molecular interactions that occur during the chromatographic process¹⁵.

EXPERIMENTAL

Preparation of the monomers

Commercial DVB (Koch-Light, Colnbrook, Great Britain) contains the isomers of EVB (41.3%, w/w) and 1,3- and 1,4-DVB (39.3 and 17.3%, w/w, respectively). The 1,4-DVB content of this mixture was increased by a method in which copper(I) chloride is used to complex 1,4-DVB and subsequently heated, to regenerate the hydrocarbon¹⁶.

The purified DVB which contains 1,3- and 1,4-DVB (20 and 70% w/w, respectively) and EVB (10%, w/w) was used for preparing most of the porous polymers in this study.

4-Vinylbenzoic acid was prepared from 4-chlorostyrene by a Grignard reaction¹⁷ and 4-vinylmethylbenzoate by esterification of the acid with diazomethane.

4-Nitrostyrene was prepared via 2-(4-nitrophenyl)bromoethane which was subsequently dehydrobrominated by refluxing with triethanolamine^{18,19}.

Others monomers (Koch-Light) and chemicals used in this work were obtained commercially and used after routine purification.

Preparation of polymers I

Polymers I were prepared from mixtures of styrene or substituted styrenes and DVB (Table I). Two suspension polymerization techniques were used. In method A, the monomers and a small amount of azobis(isobutyronitrile) (AIBN) dissolved in a solvent were suspended in water containing solid basic magnesium carbonate and stirred for 24 h²⁰, during which time the temperature was changed from 50° to 65°. The solid suspending agent was then dissolved in concentrated hydrochloric acid and the polymer beads filtered, dried and sieved. The yield of polymer beads of 60–120 mesh was between 10% and 50% of the total product.

In method B the solid suspending agent was replaced by a water-soluble non-ionic surfactant²¹. This method is the more suitable for preparing beads for chromatography since it requires lower rates of stirring, gives a higher yield of beads (> 95%) with useful mesh size (60–120) and does not require a final wash with acid (for such washing could not be used with acid sensitive groups on the polymer surface).

Preparation of polymers II

Polymers II were prepared by chemical modification of styrene- or EVB-DVB porous polymer beads (Table I). Two commercial porous polymers, Porapak Q (100–120 mesh; Waters Assoc., Milford, Mass., U.S.A.) and Chromosorb 102

TABLE I
SYMBOLS USED TO REPRESENT POLYMERS IN THIS STUDY

<i>Symbol</i>	<i>Description/composition (mole %)</i>
<i>Polymers I</i>	
SD	styrene, DVB, EVB (55, 40, 5)
SD-Br	4-bromostyrene, DVB, EVB (40, 55, 5)
SD-Ph	4-vinylbiphenyl, DVB, EVB (42, 53, 5)
SD-OMe	4-methoxystyrene, DVB, EVB (48, 47, 5)
SD-CO ₂ Me	4-carbomethoxystyrene, DVB, EVB (25, 67, 8)
SD-NO ₂	4-nitrostyrene, DVB, EVB (45, 50, 5)
ED	EVB, DVB (50, 50)
<i>Polymers II</i>	
ED/Br(Tl)	ED polymer brominated with bromine and Tl(III) acetate in CCl ₄
ED/Ac	ED polymer acetylated with acetyl chloride
ED/NO ₂	ED polymer nitrated with fuming HNO ₃
SD-Br/Br	SD-Br polymer brominated with bromine in CCl ₄
PQ/Br(Tl)	Porapak Q brominated with bromine and Tl(III) acetate in CCl ₄
C-102/Br(Tl)	Chromosorb 102 brominated with bromine and Tl(III) acetate in CCl ₄

(100–120 mesh; Johns-Manville, Denver, Colo., U.S.A.), were also chemically modified for comparison with the polymers prepared in this study.

Bromination was carried out in one of two ways, using a concentrated solution of bromine in tetrachloromethane, or using this solution to which thallium(III) acetate had been added²².

Nitration of the polymers was carried out using a mixture of acetic anhydride, acetic acid and fuming nitric acid, and acetylation by acetyl chloride in presence of anhydrous aluminium(III) chloride²³.

Analysis of monomers and polymers

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

Infrared analyses of monomers and 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.

Electron micrographs of polymers were obtained on a Cambridge S 600 scanning electron microscope, at a range of 1.5–15 kV. The material was first coated with a very thin layer of gold in a Polaron Sputter coating apparatus at 1.2 kV and 40 mA for three min using argon backfilling.

Surface areas of the polymer beads were measured using a Micromeritics 2200 apparatus and a static one-point technique. To check the values, adsorption-desorption hysteresis loops were determined for some polymers on a Carlo-Erba Sorptomatic apparatus.

Gas chromatography

All GC results were determined isothermally on Pye Series 104 chromatographs equipped with dual flame ionization or thermal conductivity detectors attached to a Goertz RE 511 recorder.

Columns were made of Pyrex glass and ranged in length from 0.42 to 1.5 m and in I.D. from 2 to 4 mm.

RESULTS AND DISCUSSION

Before we could investigate the influence of substituents on the chromatographic behaviour of porous polyaromatic beads we had to examine the reproducibility of the polymerization, and the influence of the monomer concentrations and solvent on the polymers' properties. Retention data obtained on commercial porous polymers are known sometimes to vary from one batch of polymer to the next²⁴⁻²⁶ and these variations could limit the use of such polymers in a study of the effect of functional groups on chromatographic behaviour.

Reproducibility of polymerization methods

Four separate batches of porous polymer were prepared, using method A, from fixed proportions of styrene, EVB and DVB dissolved in diethylbenzene (DEB). The adjusted retention times of a selection of organic substrates show that the materials give reproducible retention data (Table II). Polymerization by method B also gives reproducible polymers. Thus both the polymerization methods used in this study give polymers which from batch-to-batch have closely reproducible chromatographic properties.

TABLE II

ADJUSTED RETENTION TIMES ON POROUS POLYMERS PREPARED FROM STYRENE, EVB AND DVB (26, 34 AND 40 MOLE %) WITH DEB AS SOLVENT (METHOD A) Temperature, 151°; flow-rate, 50 ml/min (nitrogen); mesh size, 100-120.

Adsorbate	Column number			
	1	2	3	4
Pentane	1.1	1.1	1.2	1.1
Hexane	2.7	2.7	2.9	2.6
Hex-1-ene	2.5	2.5	2.6	2.6
Ethanol	0.46	0.47	0.49	0.44
Propan-1-ol	1.2	1.2	1.2	1.2
Butan-1-ol	3.1	3.2	3.3	3.1
Propane-1,2-diol	4.8	5.1	5.3	5.1

Influence of polymerization conditions on the properties of polymers I

Effect of solvent on polymer surface area, pore size and HETP values. The solvents for this study were toluene, ethylbenzene (EB), propylbenzene (PB), dimethylbenzene (DMB) and DEB used in a fixed proportion of monomer to solvent [50% (v/v)]. The surface characteristics of the polymers vary with the solvent used in the preparation. Electron microscopy reveals that the pore size and the roughness of the

TABLE III

SURFACE AREA, PORE SIZE AND HETP VALUES FOR POROUS POLYMERS PREPARED FROM STYRENE, EVB, AND DVB (12, 40, AND 48 MOLE %) IN DIFFERENT SOLVENTS

<i>Solvent</i>	<i>Surface area</i> (m ² /g)	<i>Pore size*</i> (nm)	<i>HETP**</i> (mm)
Toluene	332	<<10	13.0
EB	507	<10	7.2
PB	309	50-150	6.5
DMB	543	20-80	15.0
DEB	482	50-200	3.0

* Measurements from electron micrographs.

** Using pentane at 151° and 50 ml/min nitrogen.

surface of the polymers increase with increasing molar volume of the solvent (Table III). Surface area measurements, however, do not show an inverse relationship between surface area and molar volume of the solvent as one might expect. The polymers with the largest surface areas were obtained by use of EB or DMB (Table III).

The efficiencies of the columns prepared from these polymers, as measured by HETP values using pentane, also depend on the solvent used in the polymerization (Table III).

Effect of solvent on chromatographic properties. Adjusted retention times relative to pentane for a selection of adsorbates on the polymers prepared in the different solvents are given in Table IV. Although the specific retention volumes of

TABLE IV

ADJUSTED RETENTION TIMES RELATIVE TO PENTANE ON POLYMERS PREPARED FROM STYRENE, EVB AND DVB (12, 40 AND 48 MOLE %) IN DIFFERENT SOLVENTS
Temperature, 151°; flow-rate, 50 ml/min (nitrogen); mesh size, 100-120.

<i>Adsorbate</i>	<i>Solvent</i>				
	<i>Toluene</i>	<i>EB</i>	<i>PB</i>	<i>DMB</i>	<i>DEB</i>
Pentane	1.00	1.00	1.00	1.00	1.00
Pent-1-ene	0.88	0.88	0.90	0.87	0.89
2-Methylbutane	0.88	0.82	0.88	0.87	0.83
Hexane	2.50	2.65	2.43	2.67	2.50
Hex-1-ene	2.38	2.41	2.14	2.27	2.33
<i>trans</i> -4-Methylpent-2-ene	1.94	2.00	1.86	2.00	1.94
<i>cis</i> -4-Methylpent-2-ene	1.88	1.94	1.86	1.93	1.86
2,2-Dimethylbutane	1.75	1.82	1.67	1.93	1.78
2,3-Dimethylbutane	2.00	2.18	1.95	2.20	2.11
2,2,3-Trimethylbutane	4.25	4.47	4.00	4.87	4.33
Heptane	5.88	6.18	5.81	6.07	5.78
Hept-1-ene	5.63	5.59	5.33	5.73	5.33
Ethanol	0.50	0.38	0.38	0.37	0.36
Propan-1-ol	1.19	0.97	1.02	0.97	0.97
Butan-1-ol	3.13	2.53	2.62	2.53	2.56
Specific retention volume of pentane (ml/g)	16.4	31.6	29.1	32.8	36.2

the adsorbates on the polymers are dependent on the solvent used for the polymerization, the relative retention data are almost independent of the solvent.

Clearly, the organic solvent used in the suspension polymerization is important in determining the physical characteristics of the polymer and in particular its surface and micro-pore structure. First, the solvent can participate in the polymerization as a radical chain-transfer agent²⁷. Secondly, it will, by its solvating ability, influence the conditions under which the polymer separates from the organic phase. Finally, its shape and molar volume will determine the polymers micropore structure.

The small variations in the relative retention data in Table IV most probably arise from differences in pore sizes and surface areas of the polymers accessible to the adsorbates during GC. Thus the accessible surface area for pentane and for a larger molecule will not be the same on all the polymers and should depend on the pore size of the polymer.

Since the polymers obtained when DEB was used as solvent have a large surface area and give columns with a higher efficiency than those obtained using other solvents, DEB was used for the preparation of all the chemically modified polyaromatic beads (polymers I).

Effect of monomer proportions on chromatographic properties. The effect of changing the relative proportions of the monomers in the polymerization (method A) on the retention data was studied (Table V). On increasing the proportion of styrene the relative adjusted retention times of most adsorbates are increased, in particular those of the polar molecules. This effect is relatively small and is probably caused by differing proportions of functional groups ($-\text{CH}_2\text{CH}_3$ and $-\text{CH}=\text{CH}_2$) on the surface of the polymers.

TABLE V

ADJUSTED RETENTION TIMES RELATIVE TO PENTANE ON POLYMERS PREPARED USING DIFFERENT PROPORTIONS OF MONOMERS IN DEB AS SOLVENT

Temperature, 151°; flow-rate, 50 ml/min (nitrogen); mesh size, 100-120.

Adsorbate	Styrene:EVB:DVB (mole %)			
	0:46:54	12:40:48	26:34:40	55:5:40
Pentane	1.00	1.00	1.00	1.00
Hexane	2.38	2.50	2.45	2.54
Hex-1-ene	2.09	2.33	2.40	2.42
Heptane	5.74	5.78	5.80	6.46
Ethanol	0.35	0.36	0.41	0.46
Propan-1-ol	0.96	0.97	1.09	1.23
Butan-1-ol	2.49	2.56	2.87	3.31

Elemental analyses of polymers I and II. The elemental analyses of all the polymers used in this study are recorded in Table VI. These values give a measure of the extent of chemical modification of the aromatic polymers. Thus, as expected, bromination of SD-Br with bromine in tetrachloromethane (SD-Br/Br) increases the proportion of bromine in the polymer. The values for PQ and C-102 are included in Table VI for comparison. The extent of chemical modification obtained by the

TABLE VI

ELEMENTAL ANALYSES (% w/w) OF SOME POROUS POLYMERS

See Table I for abbreviations of polymers.

Polymer	C	H	Other elements	Empirical formula
SD	91.93	8.02	—	C ₃₀ H ₃₂
SD-Br	74.86	6.41	18.73 (Br)*	C ₂₆ H ₂₇ Br
SD-Ph	92.40	7.60	—	C ₃₀ H ₃₀ Ph
SD-OMe	85.18	7.87	6.95 (O)*	C ₁₅ H ₁₅ OMe
SD-CO ₂ Me	86.19	7.40	6.41 (O)*	C ₂₄ H ₃₄ CO ₂ Me
SD-NO ₂	78.50	6.27	4.47 (N)*	C ₂₁ H ₂₀ NO ₂
SD-Br/Br	56.33	4.64	39.03 (Br)	C ₂₉ H ₂₈ Br ₃
ED	91.25	8.72	—	C ₁₅ H ₁₇
ED/Br(Tl)	66.36	6.15	27.42 (Br)	C ₁₆ H ₁₈ Br
ED/Ac	84.74	7.92	6.78 (O)	C ₁₅ H ₁₆ COCH ₃
ED/NO ₂	65.41	5.70	7.22 (N)	C ₂₁ H ₂₂ (NO ₂) ₂
PQ	90.82	8.29	—	C ₃₀ H ₃₃
PQ/Br(Tl)	74.83	6.85	18.6 (Br)	C ₂₅ H ₂₇ Br
C-102	91.98	8.03	—	C ₁₅ H ₁₆
C-102/Br(Tl)	68.82	6.01	24.3 (Br)	C ₁₇ H ₁₈ Br

* These values were obtained by subtraction of C and H values from 100.

polymerization of substituted styrenes and DVB (polymers I) is very comparable with that from derivatization of the polymers (polymers II).

*Infrared analyses of polymers I and II*²⁸. Polymers I and II were examined by infrared (IR) spectroscopy, revealing the presence of vinyl groups (3080 and 3046 cm⁻¹, =C-H stretching; and 985 and 900 cm⁻¹, =C-H deformation) in all the polymers. The IR spectra also showed that derivatization of the polymers either by bromination, acetylation or nitration reduces (but does not eliminate) these bands, with concomitant increase in IR bands corresponding to C-Br (aliphatic C-Br, 590 cm⁻¹), C-COCH₃ (C=O stretching vibrations, aryl and acyclic ketone 1682 and 1720 cm⁻¹, acetate ester 1752 cm⁻¹ and C-O stretching acetate ester 1222 cm⁻¹), C-NO₂ (Ar-NO₂, 1560, 1515, 1355 and 1340 cm⁻¹, C-O in nitroester 1655 and 1275 cm⁻¹). Thus bromination resulted in a decrease of 60 ± 5% (a baseline method was used) in absorptions associated with vinyl groups.

Bromination of the polymers with bromine in the presence of thallium(III) acetate should occur both on the vinyl groups and on the aromatic rings^{22,29}. Similarly nitration and Friedel-Crafts acetylation should be a combination of addition to the double bonds and aromatic substitution. By contrast bromination in the absence of a catalyst will occur only at the double bonds and the functional groups on the polymers prepared from 4-substituted styrenes and DVB will only be attached to the aromatic rings. These changes are clearly seen by comparing the corresponding IR spectra.

Since IR spectroscopy shows that chemical derivatization of the polymers does not remove all the vinyl groups we conclude that the reactions are only effective for vinyl groups on the polymer surfaces that are accessible to chemical reagents. Consequently the unreacted vinyl groups are in the lattices of the polymers and should be unimportant in GC.

Thermal analyses of polymers I and II. Although differential thermal analysis shows that samples of the two commercial polymers (PQ and C-102) decompose at about 240°, polymers I prepared by either method A or B and polymers II, except the two nitro-polymers SD-NO₂ and ED-NO₂, were stable (*i.e.* they neither melted nor depolymerized) below 400°. The nitro-polymers decomposed at *ca.* 330°, possibly due to self-oxidation.

The marked improvement in the thermal stability of the commercial polymers on bromination is reported in a following paper³⁰.

Surface areas and HETP values of polymers I and II. The surface areas of most of the polymers used in this study are recorded in Table VII together with HETP values of columns prepared from these packing materials. The latter values which were obtained under standard conditions using pentane were not optimised by varying the gas flow-rate.

Electron microscopy showed that the surfaces of all the polymers of type I were similar and typical of materials (described above) prepared in DEB.

TABLE VII
SURFACE AREAS AND HETP VALUES OF SOME POROUS POLYMERS

<i>Polymer</i>	<i>Surface area (m²/g)</i>	<i>HETP (mm)*</i>	<i>Temperature (°C)</i>
SD	223	25.0	151
SD-Br	424	7.3	151
SD-Ph	372	10.4	151
SD-OMe	433	1.4	151
SD-CO ₂ Me	494	3.0	151
SD-NO ₂	81	2.3	151
SD-Br/Br	392	6.2	151
ED	504	2.1	140
ED/Br(Tl)	484	2.4	140
ED/Ac	440	2.4	140
ED/NO ₂	354	1.2	140
PQ	660**	3.2	140
PQ/Br(Tl)	—	3.7	140

* HETP values were obtained using pentane at 151° or 140° and a nitrogen flow-rate of 50 ml/min.

** Ref. 31.

Effect of sample size on retention time

In adsorption chromatography, the adsorption isotherm becomes non-linear and the retention volume is decreased with increasing adsorbate concentrations³². However, linear and satisfactory separations are obtained if small sample sizes of adsorbates are used, the sample size to produce a linear isotherm depending on the nature of adsorbent and adsorbate.

The non-linearity of the isotherm originates in three ways (i) a contribution from the saturation of the adsorbent surface by adsorbed sample, (ii) changing interactions between sample molecules and adjacent adsorbate molecules, (iii) adsorbent surface heterogeneity³³. Non-linear isotherms have also been reported for porous polymers³⁴ and the retention times on the polymers prepared in this work vary con-

TABLE VIII
ADJUSTED RETENTION TIMES RELATIVE TO PENTANE OF SOME ADSORBATES ON POROUS POLYMERS
Temperature, 140°; flow-rate, 50 ml/min (nitrogen).

Adsorbate	Polymer													
	ED/Br(TI)	ED/Ac	ED/NO ₂	PQ	C-102	C-102/Br(TI)	SD	SD-Br	SD-Ph	SD-O-Me	SD-CO ₂ Me	SD-NO ₂	SD-Br/Br	
Pentane	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	
Hexane	2.70	2.71	3.20	2.71	2.57	2.86	2.84	2.90	2.57	2.60	2.86	2.86	3.03	
Heptane	7.13	7.14	10.2	7.28	6.42	8.32	7.40	8.44	6.67	6.76	8.00	8.07	8.79	
Octane	16.2	18.6	31.9	20.5	16.2	24.6	19.2	24.1	17.0	17.82	22.0	22.8	25.7	
Benzene	3.10	3.89	5.38	3.21	3.15	3.30	3.94	3.43	4.03	3.50	3.60	5.23	3.56	
Butan-1-ol	3.53	6.86	22.7	2.90	2.77	3.34	4.39	6.37	5.72	6.20	4.58	8.79	4.83	
2-Methylpentan-2-ol	10.7	15.1	76.5	11.33	8.31	10.4	12.7	16.6	12.2	12.2	14.1	26.2	15.9	
Pentan-2-one	5.40	7.00	31.6	4.50	4.19	6.28	6.32	7.74	6.94	5.98	6.18	14.8	7.83	
1-Iodobutane	8.33	17.1	22.7	12.4	13.5	16.5	17.7	9.19	18.3	15.3	16.5	28.0	9.97	
1-Nitropropane	5.83	9.70	30.6	4.64	4.92	6.75	7.74	7.96	9.24	7.26	7.78	20.5	8.89	
Pyridine	9.40	12.2	58.5	5.19	5.65	7.49	10.4	13.0	18.4	8.46	9.58	22.1	11.8	
Specific retention volume (151°) of pentane (ml/g)	--	--	--	54.2	26.3	31.5	27.0	38.5	36.7	26.1	50.3	35.9	31.0	

siderably with sample size. Increasing the sample size resulted in a decrease of retention time. However, reproducibility was excellent when the following procedure was adopted. Injections of liquids and solutions were made by dipping the tip of a 1- μ l syringe needle into the sample for one second and immediately injecting the sample without altering the plunger position from zero. This means that only sample that was entrapped by capillary action between the barrel and the plunger was injected.

Chromatographic behaviour

Symmetrical peaks were obtained for almost all adsorbates on polymers I and II except for carboxylic acids and some alcohols which showed peak tailing on all columns except SD-NO₂ and the brominated polymers (SD-Br/Br and ED/Br). A similar behaviour has been observed on bromination of PQ and C-102 (ref. 30). This reduction in peak tailing after bromination suggests that in part the tailing arises from a specific interaction between the hydroxyl group of the adsorbate and the vinyl group on the polymer surface. In agreement with these findings Hertl and Neumann who reacted Chromosorb 102 with hydrogen fluoride found improved peak shapes for acids and amines¹⁰.

Adjusted retention times relative to pentane or benzene for a selection of compounds are given in Tables VIII and IX. These values reveal the similarities in the chromatographic behaviour of the commercial polymers, PQ and C-102, and the corresponding material SD prepared in this study. The effect of substituents on the chromatographic properties of polymers I is relatively small. These results emphasise the dominant role of the interactions with the polyaromatic lattice in determining the retention times on all polymer I materials for only where the substituent is strongly polar (SD-NO₂) is its influence clearly observed.

The substituents on polymers II have a more marked effect than on polymers I and again the nitro-polymer (ED/NO₂) is the most polar material. The origin of the

TABLE IX

ADJUSTED RETENTION TIMES RELATIVE TO BENZENE OF SOME ADSORBATES ON POLYMERS I

Temperature, 220°; flow-rate, 50 ml/min (nitrogen).

<i>Adsorbate</i>	<i>Polymer</i>						
	<i>SD</i>	<i>SD-Br</i>	<i>SD-Ph</i>	<i>SD-OMe</i>	<i>SD-CO₂Me</i>	<i>SD-NO₂</i>	<i>SD-Br/Br</i>
Benzene	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Toluene	1.85	2.29	1.89	1.93	1.96	1.87	2.00
Nitrobenzene	11.1	13.3	11.5	11.0	12.1	20.7	14.3
2-Nitrotoluene	16.3	20.7	16.6	16.6	18.2	29.2	22.3
3-Nitrotoluene	19.9	26.9	20.7	19.7	22.1	39.9	29.9
4-Nitrotoluene	22.5	30.6	23.6	22.3	25.9	46.4	34.4
Phenol	5.54	6.29	5.79	6.00	6.52	10.8	5.75
2-Cresol	8.77	10.0	9.05	9.43	10.5	15.5	9.44
3-Cresol	9.85	11.7	10.2	10.7	12.4	19.6	11.4
4-Cresol	9.85	11.9	10.2	10.7	12.3	19.4	10.9
Aniline	5.23	6.86	5.89	6.57	6.81	—	5.88
Specific retention volume of benzene (ml/g)	14.7	19.1	17.7	18.7	25.5	21.0	16.7

difference in the polarities of polymers I and II, which chemical analyses show to be chemically modified to similar extents, probably lies in the fact that in polymers I the substituents are dispersed throughout the lattice of the polymer whereas with polymers II the substituents are on the surface of the polymer and more accessible to the adsorbates. The nature of the interaction between adsorbate and porous polymer will be discussed in a following paper¹⁵.

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