

TAILORING POROUS POLYMER GAS CHROMATOGRAPHIC PACKINGS

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SUMMARY

The synthesis, thermal stabilities, B.E.T. surface areas and maxima of the pore radii distributions of some porous polymers were studied. The specific retention volumes of selected compounds were measured and McReynolds constants were calculated, providing a classification of polymers for gas chromatographic purposes. The effects of the chemical nature, surface area and porous structure of the polymers on the retentions of solutes with different polarities were determined. Examples of the practical analytical utilization of these stationary phases are presented.

INTRODUCTION

Since Hollis¹ and Hollis and Hayes^{2,3} reported the development of porous polymers as stationary phases for gas chromatography (GC), a number of such products have become commercially available and are now widely employed as column packing materials. However, it should be possible to prepare further porous polymers that possess particular properties that are suitable for the separation of different types of compounds. A suitable choice of the functional groups that can be incorporated into the polymer skeleton by the addition of certain monomers, and careful control of the surface area and the porosity during the synthesis of these polymers, make it possible to obtain tailor-made materials for particular applications.

The purpose of this study was to show that the chemical nature, pore size and pore volume exert a considerable influence on the performance of gas chromatographic columns and can be optimized.

The efficiency of a chromatographic separation depends on the retention time of the substances involved and the width of the peaks. In the Kubín and Kučera theory of gas-solid chromatography (GSC)⁴⁻⁶, these two parameters are defined as the first absolute moment, μ_1 , and the second central moment, μ_2 , of the chromatographic curve. If the conditions that can be independently selected (particle diameter and flow-rate of the carrier gas) are ignored and if the adsorption is assumed to take place in the linear region of the isotherms, the first and second moments are functions

of the quantities that characterize the chemical nature and texture of a solid packing as follows⁷:

$$\mu_1 = f_1(K_A) \quad (1)$$

$$\mu_2 = f_2(K_A, k_{ads}, \beta, D_{int}^{-1}) \quad (2)$$

where K_A denotes the adsorption equilibrium constant, k_{ads} the adsorption rate constant, β the internal porosity of the particles and D_{int} the effective diffusion coefficient of the separated substances in the pores of the solid.

For the purpose of tailoring a polymeric packing, the relationships between K_A , k_{ads} , β or D_{int} and structural and textural variables have to be considered. The distance of the peak from the start on a chromatogram increases with increase in the adsorption equilibrium constant, K_A , which depends on the strength of the interaction of the solute with the solid phase. This interaction may vary from a weak Van der Waals attraction to chemical bonding caused by hydrogen bonds, a charge-transfer complex or metal complex formation. Polymeric packings offer the possibility of affecting the strength of the interaction by attaching suitable functional groups to the macromolecular skeleton. Even finer modifications of adsorptivity of a given functional group by electronic effects due to different bridges inserted between the group and the polymer chain can be imagined. The choice of the functional groups can be based on both experience with various stationary phases used in gas-liquid chromatography (GLC), characterized by the vague term of polarity, and the more fundamental classification of substances according to their ability to form a hydrogen bond⁸ or to act as coordinating solvents⁹. The chemical nature of the porous polymer will be most effective for the separation if it possesses a highly orientated (homogeneous) surface that offers only a single type of group for interaction with the solute. Then, the differences in the K_A values for solutes with different chemical structures will be large. If more than one type of group is available on the surface, the selectivity of the separation of chemically different solutes may be diminished. However, in homologous series of organic compounds when steric effects are absent, K_A should increase with increasing molecular weight, irrespectively of the quality of the surface.

Strong adsorption invariably increases the peak width, as is apparent from eqn. 2 (where K_A is involved) and as is confirmed by experience. Thus, improved separations of different classes of compounds achieved as a result of large differences in retention times are offset by poorer separations of members of the same class due to broadening of the peaks. The effects of the chemical nature of the solute on the k_{ads} value are difficult to predict. However, its effect on peak width is small⁷. The same applies to β , which can be varied only in a narrow range.

Thus, the principal means of independently influencing the peak width already in the synthesis of polymeric packings consists in the regulation of its pore system. In narrow pores, Knudsen diffusion prevails (collisions of molecules with the walls are more frequent than collisions between molecules), and its rate increases linearly with increasing pore diameter. In broad pores, the rate of diffusion is independent of the pore diameter and the effective diffusion coefficient is proportional to the bulk diffusion coefficient. Fig. 1 shows an example of the dependence of D_{int} on the average pore diameter calculated for conditions suitable for the chromatography of *n*-hexane with

hydrogen as carrier gas on a porous solid^{10,11}. It shows that an increase in the pore diameter by three orders of magnitude increases the diffusion coefficient by more than two orders of magnitude. Therefore, polymers with large pores should give a better performance as chromatographic packing. This has been confirmed experimentally¹².

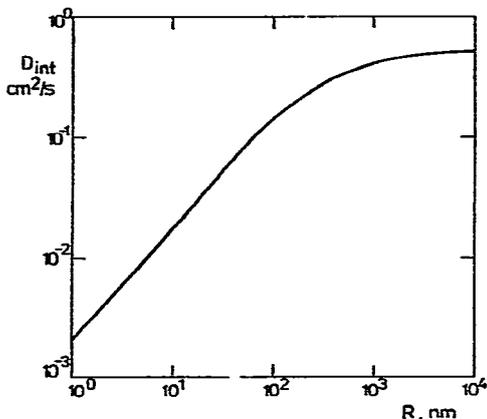


Fig. 1. Dependence of the effective diffusion coefficient, D_{int} , on average pore diameter calculated by means of the equation $1/D_{int} = 1/D_{KB} + 1/D_{AB}$ and taking the bulk diffusion coefficient $D_{AB} = 0.5148$ cm²/sec (for a hydrogen-*n*-hexane mixture) and the Knudsen diffusion coefficient $D_{KB} = 0.0202$ cm²/sec (for *n*-hexane at 10 Torr).

EXPERIMENTAL

Apparatus

The gas chromatographic measurements were carried out with a Pye Model 64 heated dual flame-ionization detector programmed chromatograph (Series 104, Pye Unicam, Cambridge, Great Britain). It was equipped with a 0-1-mV recorder (Honeywell, Elektronik 194). The columns employed were 170 × 0.4 cm I.D. glass tubes and nitrogen was used as the carrier gas at a flow-rate of approximately 30 ml/min. The samples were introduced with a 10- μ l Hamilton microsyringe. The injection port and detector temperatures were maintained at 200°.

The thermal stabilities of polymers were determined gravimetrically using the simplified quartz spring sorption balance of McBain and Bakr¹³. The sensitivity of the spring was 10 mg/mm and the temperature was increased at a constant rate of about 1°/min. Steadily flowing nitrogen was used instead of evacuation. The changes in the weight of the resin were followed with a cathetometer (Pye) with an accuracy of ± 0.05 mm.

The adsorption measurements were performed with a Sorptomat 1826 apparatus (Carlo Erba, Milan, Italy) equipped with a digital reduction unit.

Chemicals

Benzene, pyridine, methanol, ethanol, 1-butanol, 1,4-dioxane, 2-butanone, acetic acid, *n*-butyl acetate and nitromethane (all reagent grade, except nitromethane) were supplied by Lachema (Brno, Czechoslovakia). Ethylene dimethacrylate and 2-

hydroxyethyl methacrylate (both pure) were products from Dental (Prague, Czechoslovakia), and benzoyl peroxide from Argon (Lodź, Poland). *n*-Hexane, *n*-octane, *n*-nonane, *n*-decane (all 99.4–99.8%, GC analysis), 1-nitropropane, 2-pentanone (both at least 97%, GC analysis), 4-vinylpyridine, N-vinyl-2-pyrrolidone and α,α' -azobisisobutyronitrile (all pure, GC analysis), were supplied by Fluka (Buchs, Switzerland). Methane (purity at least 99%), was supplied by Schuchardt (Munich, G.F.R.) and *n*-heptane (reagent grade) by VEB Jenapharm-Laborchemie (Apolda, G.D.R.). Squalane was a product of May & Baker (Dagenham, Great Britain), while 1-iodobutane, 2-methyl-2-pentanol, divinylbenzene (40%) and *cis*-hydrindane were from our laboratory stock. 2-Cyanoethyl methacrylate was synthesized according to the literature^{14,15}.

Preparation of porous polymers

Poly[(2-cyanoethyl)methacrylate] (CEM) was prepared¹⁶ by copolymerization of 2-cyanoethyl methacrylate with ethylene dimethacrylate using *n*-butyl acetate as a diluent and benzoyl peroxide as initiator at 68–70°.

Poly[(2-hydroxyethyl)methacrylate] (HEM) was synthesized from 2-hydroxyethyl methacrylate and ethylene dimethacrylate with xylene as diluent at 90°.

Poly(4-vinylpyridine) (PYR) was obtained by polymerizing 4-vinylpyridine with divinylbenzene in *n*-heptane at 80°.

Poly(N-vinylpyrrolidone) (PON) was prepared by copolymerization of N-vinyl-2-pyrrolidone in *n*-heptane at 75–80°.

In the last three instances, α,α' -azobisisobutyronitrile was used as initiator of the polymerization. The resulting products were crushed and fractionated on sieves and the fraction of particle size 0.2–0.4 mm was extracted with methanol for 16 h and dried at elevated temperature.

The B.E.T. surface area was measured with nitrogen at the temperature of liquid nitrogen and the pore distribution was calculated from the desorption branch of the isotherm using the Roberts¹⁷ method. The results are summarized in Table I.

TABLE I

B.E.T. SURFACE AREAS AND MAXIMA OF PORE RADII DISTRIBUTIONS OF POROUS POLYMERS UNDER STUDY

Polymer	<i>S</i> (m ² /g)	Most frequent pore radii (nm)
HEM	15	51
CEM	24	76 ¹²
PYR	51	80
PON	50	58

Column packings and specific retention volumes

The fractions of individual porous polymers of particle size 0.2–0.4 mm were chosen as column packings. Amounts of 10.10 g of CEM, 8.75 g of HEM, 5.85 g of PYR and 4.90 g of PON were pre-conditioned for 16 h at 160° with the carrier gas flowing and used both for determining the retention volumes of selected substances and for calculating McReynolds constants¹⁸ at 142° in all instances.

RESULTS AND DISCUSSION

A series of polymer packings was synthesized based on commercial or specially prepared monomers and suitable crosslinking agents. Special care was taken to develop a polymerization procedure that would yield materials with a relatively low surface area and broad pores; some results on the relationships between surface area and pore size distributions have been reported previously¹². The monomers were selected according to their expected ability to associate with various solutes by means of hydrogen bonds (HEM), proton-accepting coordination (CEM, PYR) or charge-transfer complexing (PON).

Firstly, their thermal stabilities were measured thermo-gravimetrically and Fig. 2 shows a graph of loss of weight *versus* temperature. PYR was found to be the most stable polymer, being usable up to 250°; higher temperatures can be tolerated during a temperature-programmed run. The upper limit for HEM and PON was *ca.* 220°; the value for HEM is in accordance with a literature report¹⁹ for a similar material. The relatively low thermal stability of CEM has been mentioned previously²⁰.

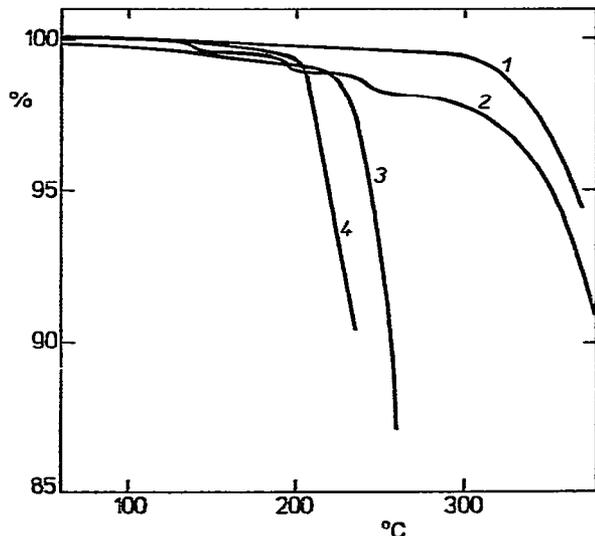


Fig. 2. Plot of loss of weight of porous polymers *versus* temperature. Heating rate, *ca.* 1°/min. 1 = PYR (0.29630 g); 2 = PON (0.20610 g); 3 = HEM (0.29600 g); 4 = CEM (0.77728 g).

The traditional classification of GC stationary phases according to their polarity is vague and, in general, "polarity" is an ill-defined term because various solvation (in GLC) or adsorption (in GSC) mechanisms are neglected. The concept of polarity is usually derived from the affinity of a given substance for another (polar) substance. Therefore, the McReynolds constants (ΔI), which provide the best information about the selectivity of various stationary phases, were used in this study. An advantage of these constants is their clear physical meaning as the relative adsorption equilibrium constants $\Delta I \approx \log(K_A^X/K^{\text{squalane}})$ of a solute A on a stationary phase X with respect to a standard (20% loading) squalane stationary phase. Table II shows

the values of ΔI on our polymer packings arranged according to decreasing adsorption ability towards polar compounds, which was defined as the average of the ΔI values for the first five substances listed in Table II. It is evident that PON can be considered to be the stationary phase with the highest polarity. It is worth noting that the McReynolds constants differ significantly from those obtained on the other investigated stationary phases. Therefore, PON is not suitable for the separation of related substances but it is of use in fractionating groups of compounds. On the basis of the capability of charge-transfer complex formation between the pyrrolidone functional groups chemically incorporated on to the polymer matrix and aromatic compounds, PON was successfully used¹² for determining trace amounts of non-aromatics in aromatic hydrocarbons. HEM and CEM showed comparable adsorption abilities in spite of the different natures of their functional groups and assumed adsorption mechanisms. Different behaviour was shown by PYR; its adsorption ability was in general lower and it gave large differences in the ΔI values for some test substances.

TABLE II

SELECTED McREYNOLDS CONSTANTS AT 142°

The absolute values of the retention indices observed on the Squalane column at 142° are as follows: benzene, 692; 1-butanol, 638; 2-pentanone, 671; 1-nitropropane, 664; pyridine, 756; 2-methyl-2-pentanol, 746; 1-iodobutane, 855; 1,4-dioxane, 705; *cis*-hydrindane, 1032.

Solute	ΔI			
	PON	HEM	CEM	PYR
Benzene	3180	275	269	58
1-Butanol	5720	522	476	156
2-Pentanone	4150	372	404	166
1-Nitropropane	6000	566	603	292
Pyridine	5530	551	481	183
2-Methyl-2-pentanol	4800	—	349	208
1-Iodobutane	5230	205	188	-445
1,4-Dioxane	3640	424	450	95
<i>cis</i> -Hydrindane		-58	-19	-34

However, the McReynolds constants do not answer every question concerning the applicability of a stationary phase to practical separation problems. Therefore, the specific retention volumes of selected compounds were calculated and expressed relative to those for *n*-heptane. Their values are given in Table III together with the corresponding boiling points.

The specific retention volumes were correlated with some properties of the polymers studied. Firstly, the effect of the surface area and porosity on the retention behaviour was investigated. With compounds, the sorption of which is predominantly due to non-specific interactions²¹, the retention volumes depend primarily on surface area (see Tables I and III). However, the retention volumes of *n*-alkanes on CEM are smaller than those on HEM although their surface areas are reversed. This probably results from the fact that HEM possesses about 20% of its total surface area in pores smaller than 5 nm, whereas no microporous structure was found with CEM²². If specific interactions (*e.g.*, hydrogen bonding or complex formation) between the component and the adsorbent are expected to be the main contribution to the adsorption,

TABLE III

SPECIFIC RETENTION VOLUMES OF SELECTED COMPOUNDS ON SOME POROUS POLYMER PACKINGS AND SQUALANE

Temperature, 142°; carrier gas, nitrogen.

Compound	B.p. (°C)	Specific retention volume				
		HEM	CEM	PYR	PON	Squalane
<i>n</i> -Hexane	68	0.61	0.60	0.53	0.67	0.52
<i>n</i> -Heptane	98.4	1.00	1.00	1.00	1.00	1.00
<i>n</i> -Octane	125.5	1.83	1.73	1.86	1.04	1.92
<i>n</i> -Nonane	150.8	3.11	2.30	3.55	1.09	3.60
<i>n</i> -Decane	174.1	5.44	5.07	6.51	1.13	6.64
<i>cis</i> -Hydrindane	167.7	4.78	5.47	6.55	0.67	8.48
Benzene	80.1	4.61	4.13	1.37	3.50	0.96
Pyridine	115.5	30.67	18.27	4.49	11.22	1.44
1-Iodobutane	130	7.72	6.40	0.16	10.31	2.72
Ethanol	78.5	3.67	3.73	0.96	2.05	0.20
1-Butanol	117.5	13.56	9.47	3.37	10.27	0.68
2-Methyl-2-pentanol	121.5	—	8.53	4.92	7.21	1.24
2-Butanon	79.6	4.56	5.33	1.40	2.54	0.48
2-Pentanon	102	7.00	7.60	2.37	5.27	0.84
1,4-Dioxane	101	11.33	11.73	1.88	4.31	1.04
Acetic acid	118.5	46.77	33.33	—	—	—
Nitromethane	100.8	10.50	14.93	1.76	2.85	0.28
1-Nitropropane	131	19.89	21.47	5.00	11.73	0.80
V_g (<i>n</i> -heptane) (ml/g)	—	2.27	1.65	18.33	15.49	21.45

then the relative retention is markedly increased on polymers that are capable of stronger bonding. The retentions of all polar solutes are in accord with this concept, particularly nitromethane, nitropropane and pyridine.

From a comparison of the specific surface areas and the maxima of the pore

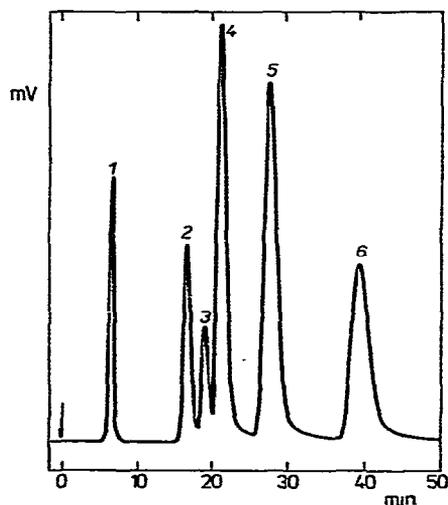


Fig. 3. Chromatogram of *n*-C₁-C₅ fatty acids and water at the optimal carrier gas flow-rate²⁰. 1 = Water; 2 = acetic acid; 3 = formic acid; 4 = propionic acid; 5 = butyric acid; 6 = valeric acid.

distribution^{23,24} of our sorbents with commercially available sorbents, it is clear that the differences in each are about one order of magnitude. The large surface area and narrower pores can be assumed to cause a relatively strong sorption of solutes on commercial packings. If reasonable retentions are to be achieved, the column has to be operated at considerably higher temperatures, even when low-boiling compounds are being analysed. However, as has already been pointed out previously¹², the chemical homogeneity of the surface may lead to a higher selectivity of our low-surface-area packings compared with commercial packings.

The porous polymers considered in this paper were tested in actual analyses. For instance, CEM was found to be a very convenient column packing for the separation of fatty acids and water^{20,25,26} (Fig. 3) and also for determining water in compounds containing carbonyl groups²⁷. PON was employed for the group analysis of trace non-aromatic fractions in aromatic hydrocarbons¹² and PYR proved excellent for the determination of water in aniline solutions with simultaneous separation of its derivatives (Fig. 4).

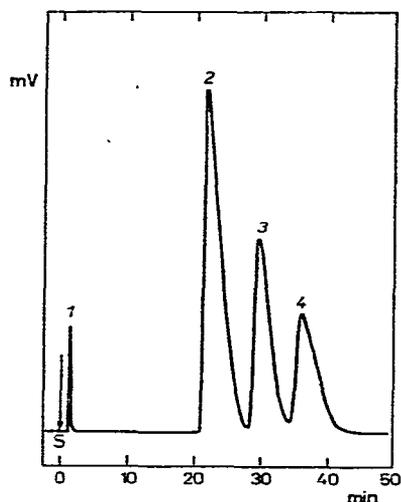


Fig. 4. Separation of water, aniline and its derivatives. Column, 170×0.4 cm I.D.; PYR, 0.2–0.4 mm; column temperature, 188° ; carrier gas (hydrogen) flow-rate, 30 ml/min. 1 = Water; 2 = N,N-dimethylaniline; 3 = aniline; 4 = N-methylaniline.

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