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POROUS BEAD POLYAROMATIC COPOLYMERS CONTAINING ESTER GROUPS

III*. PHYSICOCHEMICAL AND CHROMATOGRAPHIC CHARACTERISTICS

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SUMMARY

The basic chromatographic behaviour and physicochemical properties of porous copolymers of 4,4′-di(methacryloyloxymethyl)diphenylmethane (DMD) have been studied using these materials as column packing in gas chromatography. A range of separation abilities and sorption characters have been revealed. DMD–styrene copolymers have been found to be good universal sorbents for separation of a number of organic mixtures (including amines), with separation abilities similar to those of Chromosorb 101.

INTRODUCTION

The majority of porous polymers used as column packings are prepared by precipitation cross-linking copolymerization of vinyl monomers, with divinylbenzene and ethylene glycol dimethacrylate as a cross-linking medium. Recently a new kind of cross-linking agent, namely dimethacrylate derivatives of polycyclic hydrocarbons, has been recommended for the preparation of porous polymeric sorbents[1,2].

A series of porous bead copolymers have been synthesized in our laboratory from styrene and 4-(methacryloyloxymethyl)diphenylmethane (MD) ans monomers and 4,4′-di(methacryloyloxymethyl)diphenylmethane (DMD) as the cross-linking agent (Fig. 1)[2,3]. Every batch of copolymers was tested to determine its chromatographic behaviour. Preliminary investigations of the separation of aliphatic hydrocarbons, alcohols and other organic mixtures indicated the very poor selectivity and separation ability of most batches, and only those of macroporous structure proved to be of interest. Reasonable separation abilities were also found for MD–DMD copolymers. Since the copolymers obtained by using styrene and DMD showed the best chromatographic properties, we undertook a more detailed characterization of these materials as sorbents in gas chromatography (GC).
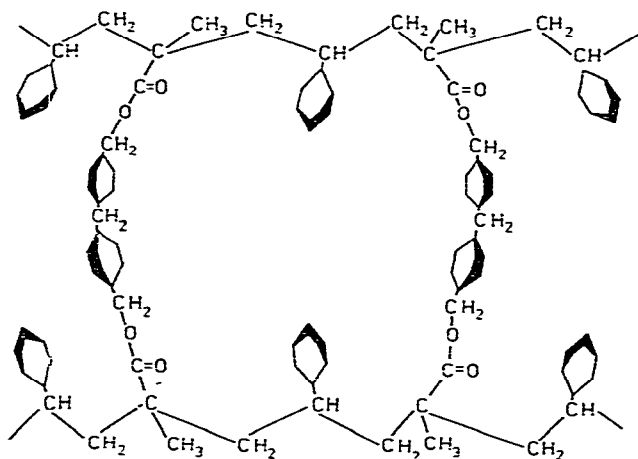
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* Part II: ref. 3.

Fig. 1. DMD–styrene copolymer.

Preparation of copolymers

The sorbents were prepared by the suspension copolymerization of DMD with styrene and of DMD with MD under conditions suitable for porous structure formation[2,3].

Chromatographic measurements

The GC measurements were carried out with a Chromatron gas chromatograph CHF·18.3 equipped with a thermal conductivity detector. Glass columns were used ranging from 1 to 1.4 m in length and from 2 to 4 mm I.D. Hydrogen was used as a carrier gas at flow-rate of 30 ml/min. The measurements were carried out at 150°C by injecting samples of 0.1–0.3 μl of various substances. The dependences of retention volume *versus* temperature characterizing the temperature transition in the copolymers were determined from chromatographic data using an electronic integrator (CDS-Varian) equipped with a computer.

Adsorption enthalpies were derived from the slope of the straight line of log V_g against $1/T$.

RESULTS AND DISCUSSION

The physical characteristics of the DMD copolymers used are listed in Table I. These copolymers (with different surface properties) were prepared by varying the nature of the monomer, diluent concentration and the degree of cross-linking. The properties of Chromosorb 101, used as a control substance, are also presented in Table I.

The reproducibility of polymerization was controlled by determination of the surface parameters as well as the chromatographic behaviour for copolymer III (Table I). Three separate batches of porous copolymers were prepared under identical conditions. The results are summarized in Table II.

TABLE I

CHARACTERIZATION OF THE DMD POROUS COPOLYMERS* AND CHROMOSORB 101

Copolymer	Composition of monomers (g)			Diluent (ml)		Specific surface area, S (m^2/g)	Mean pore radius, R_m $(Å)$	Thermal stability ($^\circ C$)
	Sty-rene	DMD	MD	n-Dode-cane	Toluene			
I	8	12	—	20	60	56	341	280
II	8	12	—	20	30	45	181	280
III	—	10	10	10	40	59	95	250
Chromo-sorb 101**	—	—	—	—	—	21	3000–4000	275

* Further details are given in refs. 2 and 3.
** Data from ref. 4.

TABLE II

REPRODUCIBILITY OF THE POROSITY PARAMETERS (S, R_m) AND CHROMATOGRAPHIC CHARACTERISTICS (V_g, HETP) OF DMD–STYRENE COPOLYMERS (SAMPLE III FROM TABLE I)

A = Benzene; B = butan-1-ol; C = pentan-2-one; D = 1-nitropropane; E = pyridine. Flow-rate: 30 ml/min. Temperature: 151°C.

Sample	S (m^2/g)	R_m $(Å)$	HETP (mm)	Specific retention volume, V_g (ml/g)				
				A	B	C	D	E
1	56	341	3.01	19.65	20.92	24.31	43.32	48.15
2	61	320	3.10	20.35	21.73	23.75	46.33	48.43
3	63	298	3.12	20.05	22.04	22.62	45.26	48.82

TABLE III

MODIFIED McREYNOLDS CONSTANTS AND GENERAL SELECTIVITY INDEX, Σ, USING GRAPHITIZED THERMAL CARBON BLACK AS REFERENCE

Temperature: 140°C. Retention index differences were calculated using the reported retention data on GTGB[5] for benzene (A), butan-1-ol (B) and pentan-2-one (C). Absolute values of the retention indices on copolymer III were: A, 826; B, 835; C, 838.

Copolymer No.	I_A	I_B	I_C	Σ
I	259	351	285	895
II	252	345	293	890
III	356	481	420	1237
Chromosorb 101	126	201	175	502

The variations in the retention data in Table II arise from differences in the pore sizes and surface areas accessible to the adsorbates during the chromatographic process. However, they indicate that the method of polymerization gives polymers having chromatographic properties which are highly reproducible from batch to batch. The polarity of the copolymers in Table I has been evaluated by means of the McReynolds indices (Table III), as proposed by Lindsay Smith *et al.*[6], using graphitized thermal carbon black as a reference.

As is seen in Table III, the retention indices indicate a much higher polarity for DMD copolymers than for Chromosorb 101, but lower than observed for 2-hydroxyethyl methacrylate–ethylenedimethacrylate porous copolymers[7] as expected. Sample III exhibits the highest polarity of all the copolymers, owing to the higher content of ester groups per polymer unit. However, this high polarity does not considerably influence selectivity. Retention index differences are largest for butanol (Table III), *i.e.*, a compound which is able to form hydrogen bonds with DMD copolymers. The results of the adsorption enthalpy measurements confirm the evident specificity of interaction between DMD copolymers and adsorbate molecules having π bonds or local positive charges:

Adsorbate	Pentane	Hexane	Cyclohexane	Benzene	Ethanol	Hexanol
H_a (kcal mol)	9.8	11.2	13.5	13.2	10.2	15.3

The above values lie between those obtained for non-specific polymeric sorbents such as Chromosorb 101, 102 or Porapak Q and specific sorbents such as Porapak T or Chromosorb 103[8].
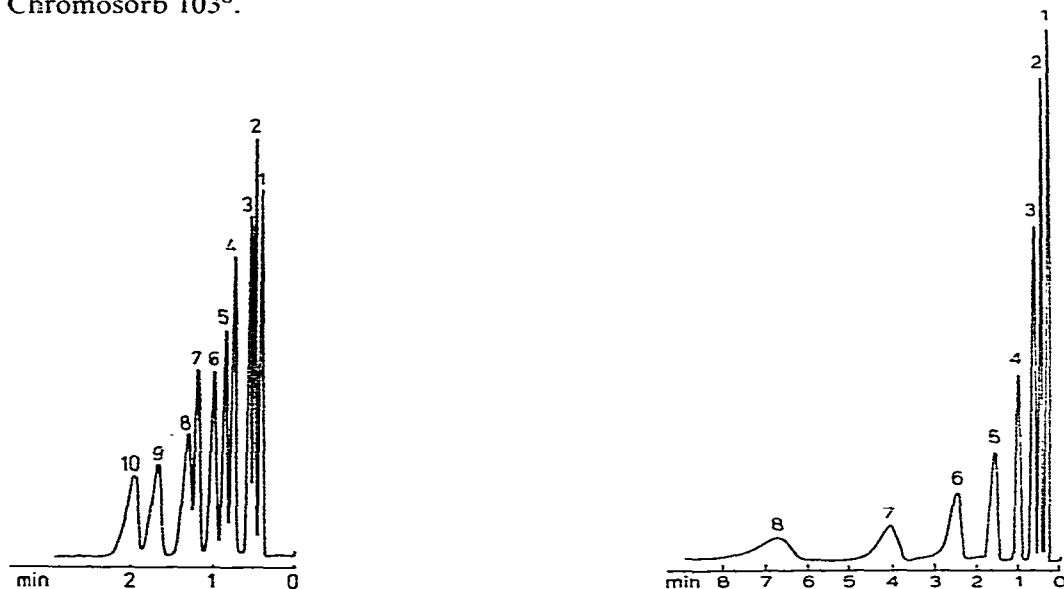

Fig. 2. Separation of alcohols. Column: 1.4 m × 2.5 mm I.D. Temperature: 151°C. Flow-rate: 30 ml/min. Peaks: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = *n*-propanol; 5 = *sec.*-butanol; 6 = isobutanol; 7 = *n*-butanol; 8 = 2-pentanol; 9 = isoamyl alcohol; 10 = *n*-amyl alcohol.

Fig. 3. Separation of aliphatic hydrocarbons. Conditions as in Fig. 2. Peaks: 1 = pentane; 2 = hexane; 3 = heptane; 4 = octane; 5 = nonane; 6 = decane; 7 = undecane; 8 = dodecane.
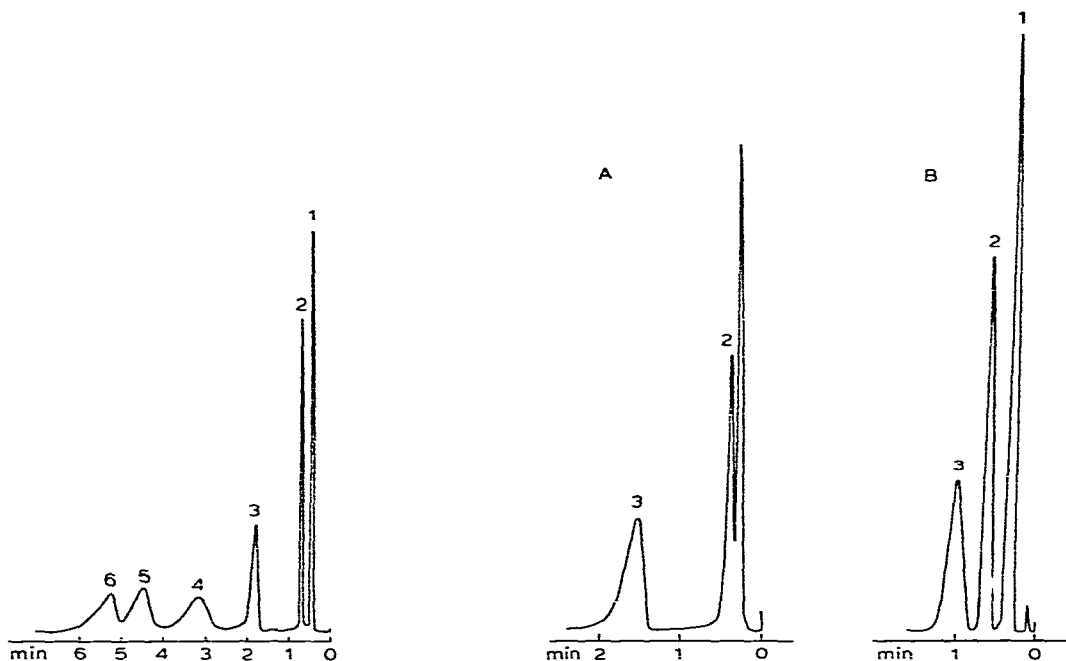
Fig. 4. Separation of ethers. Conditions as in Fig. 2. Peaks: 1 = diethyl ether; 2 = methylbutyl ether; 3 = dibutyl ether; 4 = diisoamyl ether; 5 = di-*n*-amyl ether; 6 = butyl 2,3-epoxypropyl ether.

Fig. 5. Separation of amines. Conditions as in Fig. 2. Peaks: A, 1 = dimethylamine; 2 = diethylamine; 3 = dibutylamine; B, 1 = ethylamine; 2 = diethylamine; 3 = triethylamine.

Selected chromatograms obtained with sample I are presented in Figs. 2–5. Good separations were obtained despite of the fact that the analysis conditions, *i.e.*, temperature and gas flow-rate, were not optimized. The chromatograms do not show any serious tailing. It is noteworthy that the separation temperatures are considerably lower than those on Chromosorb 101 for the same adsorbates, *e.g.*, alcohols[4]. Chromosorb 101 is known to possess a small surface area and a large pore diameter. DMD–styrene copolymers have a similar surface area but different texture. Copolymers I–III exhibit a globular grain structure[9]. The polymer nuclei of the inner part of the grain are rather closely packed and no large pores are observed. This narrow pore structure is confirmed by the differential pore size distributions of copolymers I–III, which indicate the absence of pores larger than 1000 Å. Thus, sieve effects may considerably influence the retention mechanism.

To summarize the above results, the presence of ester groups on the surface of DMD copolymers results in an excess specific interaction energy term which makes these materials particularly suitable for the separation of oxygen-containing compounds and which is responsible for their selectivity towards amines. These materials can also be used for rapid analysis of high boiling compounds.

It is known that, in the region of the glass transition of polymeric sorbents, deviations from a linear dependence of $\log V_g = f(1/T)$ can occur[10]. This effect is much stronger for a linear polymer used in the form of a thin film on a support. but
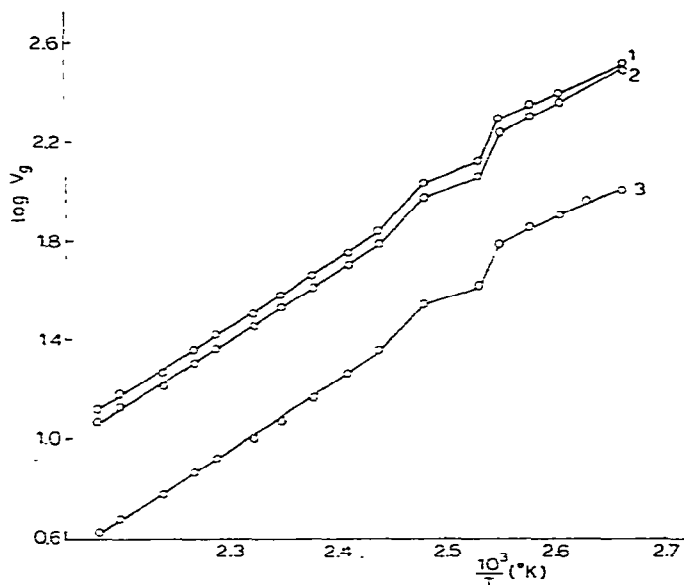
Fig. 6. Dependence of the logarithm of the specific retention volume, log V_g, of chloroform (1), benzene (2) and hexane (3) on $1/T$.

appears also when the whole sorbent is comprised by the polymer. We have found that the dependence of log $V_g = f(1/T)$ has a shape (Fig. 6) which indicates a glass transition in the range 119–121$°$C[11].

It is interesting that the observed temperature relaxation is much more prominent than was found for Spheron[7], for which only the inflexion point has been observed. This may be explained by the higher flexibility of the polyaromatic lattice and, obviously, may be connected with the lower density of the DMD copolymer. (The DMD molecule is larger than one of ethylene glycol dimethacrylate.) Thus, it is expected that, during the chromatographic process, transport (diffusion) into the bulk of the copolymer will occur more readily at temperatures higher than T_g. This diffusion effect, together with the chemical nature and texture of the grain, seems to be responsible for the chromatographic behaviour of DMD–styrene copolymers.

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