

Note

Methyl methacrylate–di(methacryloyloxymethyl)naphthalene copolymers as a column packing for gas chromatography

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Many types of polymeric materials have been introduced as column packings in gas chromatography (GC). Among these the aliphatic methacrylate polymers are well recognized in both GC and liquid chromatography (LC). Recently a new type of porous polymer has been synthesized using methyl methacrylate (MMA) and di(methacryloyloxymethyl)naphthalene (DMN) as the monomers. The latter monomer (Fig. 1) serves as a cross-linking agent for the MMA molecules, similarly to divinylbenzene which cross-links styrene molecules in the styrene–divinylbenzene copolymers.

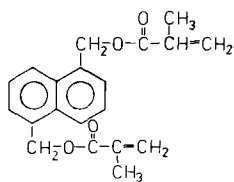


Fig. 1. Structure of DMN.

The copolymers were synthesized by the usual suspension polymerization with the use of inert components as pore-forming agents, enabling the formation of a porous structure. These materials exhibit both hydrophobic and hydrophilic character and good thermal stability, permitting their use at elevated temperatures. By varying the composition, concentration and volume of the pore-forming mixture as well as the monomer concentrations it is possible to control the specific surface area of these copolymers within the range of 1–120 m²/g.

Each sample was tested as regard its efficiency and separation ability as a column packing for GC.

EXPERIMENTAL

All chemicals were of reagent grade and used without purification. Methyl methacrylate was purified before use by distillation. Di(methacryloyloxymethyl)naphthalene was synthesized as described previously¹.

The copolymers were prepared by the suspension copolymerization of methyl

methacrylate and di(methacryloyloxymethyl)naphthalene under conditions suitable for the formation of macroporous structure^{2,3}. The inert components used to control the internal structure of the copolymers were toluene and isooctane or toluene and dodecane. Polymerization was carried out under a nitrogen atmosphere. The toluene and dodecane or toluene and isooctane mixture containing MMA, DMN and α,α' -azobis(isobutyronitrile) was suspended in an aqueous solution containing 2% of poly(vinyl alcohol) and stirred at 80°C for 10 h. The products were washed with a large volume of hot water and then extracted in a soxhlet apparatus with acetone, benzene and methanol. After drying in a vacuum desiccator, the 0.15–0.2 mm particle fraction was separated for further use.

The specific surface areas and pore volumes of the copolymers were measured with a Sorptomatic 1800 apparatus (Carlo Erba, Milan, Italy) by the BET method using nitrogen at the temperature of liquid nitrogen.

The average pore radius, \bar{r} , was calculated as:

$$\bar{r} \text{ (nm)} = \frac{\text{Pore volume (cm}^3\text{/g)}}{\text{Specific surface area (m}^2\text{/g)}} \cdot 2 \cdot 10^3$$

Pore-size distributions were calculated from the sorptomatic data according to Barret *et al.*⁴ and Wheeler⁵. Analysis of the unreacted double bonds was carried out according to Das⁶ by reaction in a non-aqueous medium with mercuric acetate further titrated by a strong acid.

The GC measurements were carried out with a Chromatron G.C.H.F 18.3 apparatus equipped with a thermal conductivity detector and glass columns (1.2 m \times 0.3 mm I.D.). Hydrogen was used as the carrier gas at a flow-rate of 40 ml/min; the bridge current was 200 mA and the temperature of the injector was 200°C. The volume of the injected samples was 0.1–0.3 μ l.

RESULTS AND DISCUSSION

Three samples of MMA–DMN copolymers with different surface properties have been selected for GC evaluation. Table I indicates their compositions and surface properties and Fig. 2 presents their differential pore-size distribution curves.

TABLE I
CHARACTERIZATION OF COPOLYMERS I–III

No.	Composition of the monomer mixture (% w/w)		Composition of the inert phase (% v/v)		Specific surface area (m ² /g)
	MMA	DMN	Isooctane	Toluene	
I	50	50	12.5	87.5	40.6
II	40	60	16.6*	83.4	81.5
III	40	60	21.5	78.5	118.0

* Dodecane was used instead of isooctane.

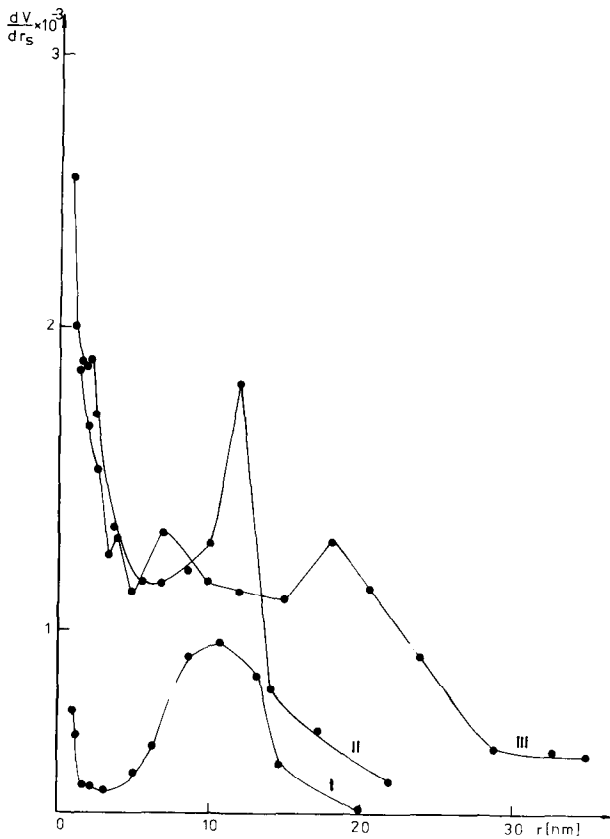


Fig. 2. Differential pore-size distribution curves of copolymers I-III.

All the copolymers contained micropores, *i.e.*, pores smaller than 4 nm, although their volumes are relatively small and copolymer III is also characterized by the presence of macropores.

In order to estimate the relative polarities of the copolymers, the retention

Specific pore volume (cm^3/g)				Average pore radius (nm)	Residual double bonds ($\mu\text{mol/g}$)	Initial decomposition temperature ($^{\circ}\text{C}$)
Micropores ($\bar{r} < 4 \text{ nm}$)	Mesopores ($4 \text{ nm} < \bar{r} < 40 \text{ nm}$)	Macropores ($\bar{r} > 40 \text{ nm}$)	Total			
0.012	0.108	—	0.12	11.5	0.056	250
0.034	0.176	—	0.21	10.2	0.023	260
0.047	0.353	0.12	0.40	6.8	0.068	260

TABLE II
RETENTION INDICES AT 175°C MEASURED ON MMA-DMN COPOLYMERS I-III, PORAPAK T AND CHROMOSORB 103

<i>Compound</i>	<i>Copolymer I</i>	<i>Copolymer II</i>	<i>Copolymer III</i>	<i>Chromosorb 103</i>	<i>Porapak T</i>
Methanol	565	530	470	474	—
Ethanol	670	628	515	514	564
Propanol-1	770	728	645	620	678
Butanol-1	870	832	760	726	780
Acetic acid	985	872	775	—	795
Propionic acid	1090	975	878	—	903
Acetone	655	665	470	547	603
Methyl ethyl ketone	725	735	590	654	702
Benzene	812	774	715	718	720
Ethyl acetate	750	725	651	650	688
Acetonitrile	760	730	680	—	639

TABLE III

SPECIFIC RETENTION VOLUME, V_g , AND COLUMN EFFICIENCY, HETP, MEASURED ON MMA-DMN COPOLYMERS*

Adsorbate	Copolymer I		Copolymer II		Copolymer III	
	V_g (cm^3/g)	HETP (cm)	V_g (cm^3/g)	HETP (cm)	V_g (cm^3/g)	HETP (cm)
<i>n</i> -Pentane	2.30	0.29	3.44	0.59	5.88	0.31
<i>n</i> -Hexane	3.45	0.25	5.50	0.47	9.40	0.22
<i>n</i> -Heptane	5.06	0.30	8.94	0.59	17.05	0.41
<i>n</i> -Octane	0.90	0.33	11.35	0.61	21.75	0.45
Methanol	3.45	0.12	4.47	0.31	1.76	0.68
Ethanol	4.37	0.17	6.88	0.13	3.52	0.45
Propanol-1	6.90	0.17	10.66	0.11	10.58	0.19
Butanol-1	11.73	0.14	18.23	0.12	22.34	0.21
Acetone	3.68	0.22	6.88	0.17	7.05	0.23
Methyl ethyl ketone	4.20	0.24	7.15	0.16	7.33	0.22
Benzene	9.66	0.17	13.76	0.26	18.81	0.21
Toluene	15.18	0.17	24.08	0.27	34.10	0.19

* Column temperature: 175°C. Carrier gas: hydrogen. Flow-rate: 40 ml/min.

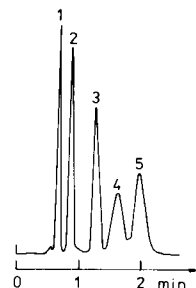
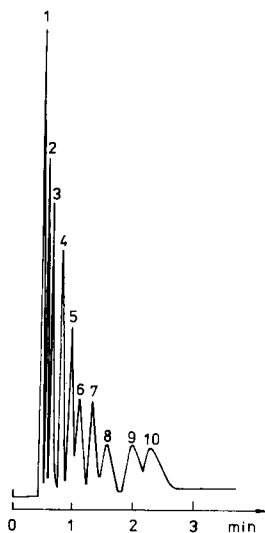


Fig. 3. Separation of alcohols on copolymer II. Column: 1.2 m \times 3 mm I.D. Temperature: 175°C. Flow-rate: 40 ml/min. Peaks: 1 = methanol; 2 = ethanol; 3 = isopropanol; 4 = *n*-propanol; 5 = *sec.*-butanol; 6 = isobutanol; 7 = *n*-butanol; 8 = pentanol-2; 9 = 3-methylbutanol-1; 10 = pentanol-1.

Fig. 4. Separation of acetates on copolymer I. Conditions as in Fig. 3. Peaks: 1 = methyl acetate; 2 = ethyl acetate, 3 = propyl acetate; 4 = isobutyl acetate; 5 = *n*-butyl acetate.

indices of several sorbates were established and compared with those of commercially available polymeric packings⁷. The Kováts retention indices measured on MMA-DMN copolymers, Porapak T and Chromosorb 103 are summarized in Table II. They are lowest for copolymer III, whose values are intermediate between those on Chromosorb 103 and Porapak T, both being strongly polar materials.

Naturally, polar groups at the effective polymer surface, such as unreacted double bonds, ester and aryl groups, have large contributions to the polarity of the polymer surface. Copolymer I is the most polar, which may in part be explained by a slightly higher methyl methacrylate content per polymer unit. However, the differences in the polarities of copolymers I-III may be due to effects other than the different distributions of the polar groups on the surface, *e.g.*, different synthesis parameters or entrapping of the suspending agent in the polymer structure.

The column efficiencies expressed as the height equivalent to a theoretic plate (HETP) and specific retention volumes are listed in Table II. As expected, the specific retention volumes of the non-polar sorbates, aliphatic hydrocarbons, increase with increasing specific surface area of the packing. This is also true for polar sorbates, in spite of the different results for alcohols on copolymer II. Naturally there is a great possibility of specific interaction with the polymer surface and this effect is expected to be larger for more polar surface of samples I and II and smallest for sample III. It is also of note that, according to the studies of Zado and Fabecic⁸, on polymers such as Porapak T, repulsive interactions occur with substances having free electron pairs. The HETP values vary within a relatively narrow range and are correlated to the differences in pore structure. Generally, the lowest HETP values are observed for copolymer I with the lowest content of micropores and with the most uniform pore

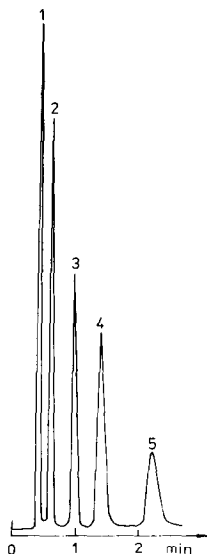


Fig. 5. Separation of aldehydes on copolymer I. Conditions as in Fig. 3. Peaks: 1 = acetaldehyde; 2 = propanal; 3 = butanal; 4 = pentanal; 5 = hexanal.

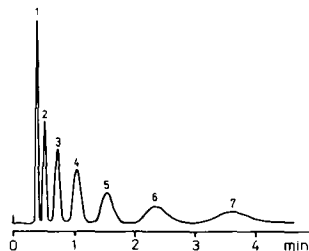


Fig. 6. Separation of aliphatic hydrocarbons on polymer I. Conditions as in Fig. 3. Peaks: 1 = pentane; 2 = hexane; 3 = heptane; 4 = octane; 5 = nonane; 6 = decane; 7 = undecane.

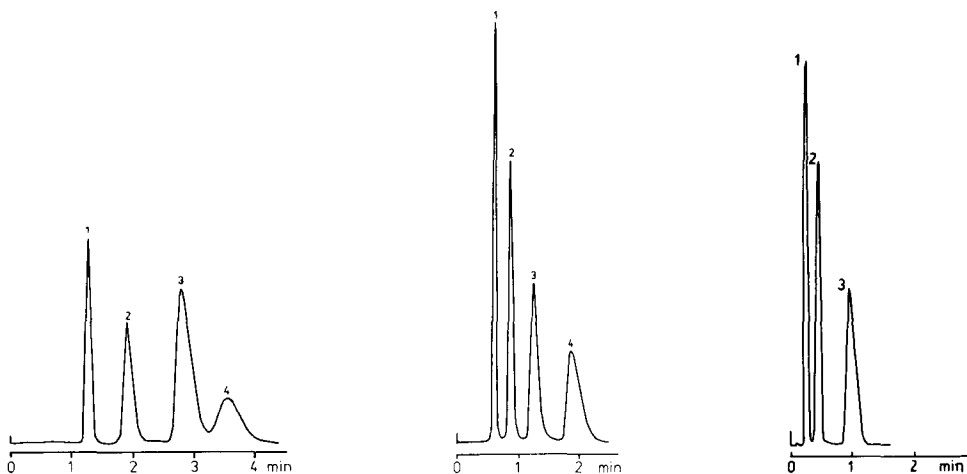


Fig. 7. Separation of aromatic compounds on polymer I. Conditions as in Fig. 3. Peaks: 1 = benzene; 2 = toluene; 3 = *o*-xylene; 4 = *p*-xylene.

Fig. 8. Separation of ketones on polymer II. Conditions as in Fig. 3. Peaks: 1 = 2-butanone; 2 = 2-pentanone; 3 = 2-hexanone; 4 = 2-heptanone.

Fig. 9. Separation of ethers on polymer III. Conditions as in Fig. 3. Peaks: 1 = diethyl ether; 2 = dipropyl ether; 3 = dibutyl ether.

distribution (see Fig. 2 and Table III), although its specific surface area is relatively low.

Copolymer III has the highest specific surface area, a fairly high percentage of large pores and gives a somewhat lower column efficiency. This may be explained on the basis of the differences in the polarity and pore distribution of the polymers. Copolymer II exhibits the lowest HETP values for alcohols, excluding methanol. This may be related to the use of dodecane instead of isooctane as a component of the pore-forming mixture, which may result in a different pore geometry.

Copolymers I–III proved to be useful in the analysis of aliphatic alcohols, ketones, aldehydes, esters and aliphatic or aromatic hydrocarbons. Some typical chromatograms are shown in Figs. 3–9. The retention times of various compounds on copolymers I–III are considerably shorter than on other polymeric sorbents like Spherons or other methacrylate polymers⁹. This enables the possibility of operating at lower temperatures, and yields separations of higher-boiling compounds.

Fig. 10 shows the linear relationships (plot of alcohols on copolymer III is non-linear) between the carbon number and the logarithm of the retention volumes of homologous series of alkanes, *n*-alcohols, *n*-alkyl acetates and *n*-alkyl ketones on copolymers I and III. The plots reveal the influence of the polarities and porosities of the copolymers on their separation abilities: the distances between the plots for copolymer I are slightly greater than those for copolymer III. The porosity pattern of copolymer I must be more favourable than those of copolymers II and III. These data confirm previous observations for styrene polymers cross-linked with aromatic dimethacrylates where a small amount of micropores and uniformity of the pore size of small specific surfaces resulted in higher column efficiencies than for highly developed surfaces^{10,11}.

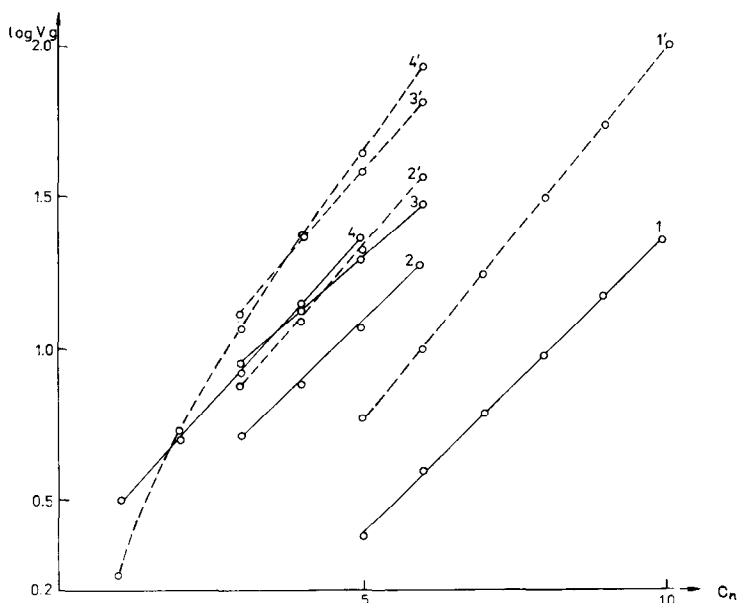


Fig. 10. Relationship between the logarithm of the specific retention volume, V_g , and the number of carbon atoms, C_n , in the molecules of the sorbates. —, Polymer I; ---, polymer III. Plots 1 = n -alkanes; 2 = n -alkyl acetates; 3 = n -ketones; 4 = n -alcohols. Conditions as in -Fig. 3.

In order better to understand the retention mechanism, I am now investigating the adsorption isotherms and heats of adsorption on these materials.

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