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EFFECT OF THE INTERNAL STRUCTURE OF MACROPOROUS POLYMERS ON THEIR CHROMATOGRAPHIC PROPERTIES

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SUMMARY

The effect of internal structure on the chromatographic properties of macroporous copolymers was studied using four types of macroporous copolymers of methyl methacrylate, 2-hydroxyethyl methacrylate and acrylonitrile crosslinked with ethylenedimethacrylate as an example. Different copolymerization parameters cause changes in the internal structure of macroporous copolymers (specific surface area, specific pore volume, submicroscopic particle size and pore distribution). It was shown that the copolymers used in the investigation contained "ink bottle" shaped pores and micropores. The main role in the retention of hydrocarbons is played by the specific surface area of the sorbents. The high content of "ink bottle" shaped pores and the asymmetry of the peaks of sorbents with a large specific surface area are probably due to the effects of porous structure on retention. The retentions of hydrocarbons and alcohols on individual sorbents correspond to differential enthalpies of sorption of the methylene group (ΔH_{CH_2}) and to polarities defined by the Kováts retention indices.

INTRODUCTION

We have shown earlier that under the conditions of gas chromatography, macroporous polymer sorbents operate, among other factors, through their specific surface area and polarity, characterized in most cases by the Kováts retention indices¹⁻³. The specific surface area of macroporous copolymers is predominantly affected by the content of the crosslinking agent and by the composition of inert components (solvent and precipitant) in the copolymerization. The polarity of macroporous copolymers can be varied by varying the type and concentration of the comonomer^{2,3}, and also by consecutive chemical transformations^{4,5} by means of which groups of various polarity are introduced into the copolymer.

It was also demonstrated that even with strongly crosslinked copolymers, adsorption or absorption interactions may become operative, depending on the temperature⁶.

By employing procedures described earlier²⁻⁵, macroporous copolymers can be prepared that differ in their internal porous structure. The way in which this internal structure of macroporous copolymers is reflected under chromatographic conditions is reported in this paper. It should be mentioned that there is much that still needs elucidation in this field, and that views differ greatly in this respect.

EXPERIMENTAL

Preparation of samples and determination of their physical properties

Four types of copolymers were prepared by suspension radical copolymerization under the conditions of formation of a macroporous structure^{7,8}: methyl methacrylate (MMA) with ethylenedimethacrylate (EDMA) in the mixture cyclohexanol-dodecanol (91:9), methyl methacrylate with 2-hydroxyethyl methacrylate (HEMA) and ethylenedimethacrylate in the mixture cyclohexanol-dodecanol (54:46) and in cyclohexanol alone, and acrylonitrile (AN) with 2-hydroxyethyl methacrylate and ethylenedimethacrylate in the mixture cyclohexanol-dodecanol (91:9).

The specific surface areas of the copolymers were determined by the thermal desorption of nitrogen with a Quantasorb apparatus (Quantachrome, Greenvale, U.S.A.) at three nitrogen concentrations and calculated using the B.E.T. equation.

The specific pore volume was calculated from the soaking values of cyclohexane determined by the centrifugation technique⁹. The fraction of micropores was determined by the capillary condensation of nitrogen.

The pore distribution was calculated from porosimetric measurements with a Carlo Erba 70 H mercury porosimeter for pore radii ranging from 7.5 μm to 5 nm (up to a pressure of 175 MPa). The fraction of "ink bottle" shaped pores was determined by using the hysteresis between the dependence of the volume of squeezed-in mercury on pressure with increasing and decreasing pressure. The pressure with increasing and decreasing pressure. The pressure was reduced gradually, and the mercury volume was read off after the establishment of equilibrium (*ca.* 20 min). The volume of pores filled with mercury at the end of the measurement (v_i) was used to determine the retention factor, $v_R = v_i/v$, where v is the total volume of squeezed-in mercury.

Chromatographic measurements

Before measurement, copolymer samples were conditioned by heating at 170° for 24 h. The retention times of sorbates used in the determination of specific retention volumes and Kováts retention indices were measured at 150° with a Pye Unicam apparatus on straight glass columns (120 \times 0.3 cm I.D.). Chromatographically pure test compounds (C₅-C₁₁ alkanes, benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine) were injected in amounts of 0.1 mm³.

The differential enthalpy of sorption of the CH₂ group (ΔH_{CH_2} , kJ/mole) was determined from the dependence of $\log V_o$ for alkanes and alcohols on the number of carbon atoms in standards using the relationship $\Delta H_{\text{CH}_2} = 19.15A$, where A is the slope of this dependence. The differential sorption enthalpy values of the CH₂ group were calculated by the least-squares method and determined with an average error of ± 0.75 kJ/mole.

RESULTS AND DISCUSSION

Four types of macroporous copolymers prepared by suspension copolymerization were used: poly(methyl methacrylate-co-ethylenedimethacrylate) prepared in the mixture cyclohexanol-dodecanol (ratio 91:9), poly(methyl methacrylate-co-2-hydroxyethyl methacrylate-co-ethylenedimethacrylate) prepared in the mixture cyclohexanol-dodecanol (54:46) and in cyclohexanol alone, and poly(acrylonitrile-co-2-hydroxyethyl methacrylate-co-ethylenedimethacrylate) prepared in the mixture cyclohexanol-dodecanol (91:9). The basic properties of macroporous copolymers which affect their chromatographic behaviour are chemical composition and specific surface area. The specific surface area of copolymers prepared in this work depends predominantly on the content of the crosslinking agent and on the composition of the components of the inert mixture²; it increases with increasing content of the crosslinking agent (EDMA), and decreases with increasing content of the comonomer, the more so the more polar is the comonomer, that is, in the order MMA \geq HEMA $>$ AN. This is due to different copolymerization parameters, which affect not only the composition but also the texture of the copolymers. Owing to the different copolymerization parameters of the individual monomers, the copolymers become enriched in MMA and AN at the expense of EDMA or HEMA. The enrichment of copolymers by AN is pronounced and can be established by elemental determination of nitrogen; it amounts to 75% compared with the AN content in the monomeric mixture (Table I). Differences in the copolymerization parameters of the crosslinking agent and comonomers are responsible for the fact that the resulting copolymer does not have a statistical character, but that longer sequences of the more polar comonomer originate in the crosslinked nucleus and proceed to the surface of submicroscopic globules which form the porous structure of the copolymer¹⁰. Submicroscopic polymer particles are in this instance large, more irregular in shape (intergrown formations, clusters), and the porosity also is lower (polymer IV, Table II) than is usual with copolymers of unsaturated esters¹⁰.

The whole range of porosity of porous systems can be adequately characterized by the soaking value or sorption of compounds that do not swell the polymer network, and by mercury density. From the soaking value of cyclohexane, it is found

TABLE I
CHARACTERIZATION OF COPOLYMERS

Polymer	Composition of monomeric mixture (wt.-%)				Composition of inert phase (wt.-%)		Copolymer composition, determined* / calculated**			Grain size (μm)
	MMA	HEMA	AN	EDMA	Cyclohexanol	Dodecanol	C (%)	H (%)	N (%)	
I	10	—	—	90	91	9	61.47 60.52	7.77 7.21	—	200-315
II	8	32	—	60	54	46	57.55 58.87	7.31 7.39	—	200-300
III	8	32	—	60	100	0	59.40 58.87	7.74 7.39	—	100-200
IV	—	55	6	39	91	9	58.15 57.28	7.35 7.37	2.83 1.61	100-200

* Elemental composition determined with the absolute errors $\pm 0.09\% \text{C}$, $\pm 0.05\% \text{H}$, $\pm 0.03\% \text{N}$.

** Calculated from the composition of the monomeric mixture.

TABLE II
POROUS STRUCTURE OF METHACRYLATE COPOLYMERS

Polymer	Specific pore volume (cm^3/g)		Micropore volume (cm^3/g)	Volume of "ink bottle" shaped pores (cm^3/g)		Specific surface area (m^2/g)	R^* (nm)	r^{**} (nm)	Radius of most frequently occurring pores (nm)
	From soaking value of cyclohexane	From mercury porosimetry		From desorption of nitrogen	From mercury porosimetry				
I	1.828	0.938	0.014	0.229	0.431	196	14	19	38
II	1.963	—	—	0.140	—	95	29	41	—
III	1.079	—	—	0.206	—	107	25	16	—
IV	0.803	0.538	0.020	0.091	0.151	57	48	19	20

* Mean radius of submicroscopic particles calculated using ref. 10 for polymer density 1.1.

** Mean pore radius calculated using ref. 10.

that the total porosity of the copolymers under investigation is 50–70 vol.%, which is much greater than with styrene–divinylbenzene copolymers, for which the highest porosity was 30%¹⁰. Hence it can be deduced that together with micropores that constitute closely arranged submicroscopic particles, there also exist pores the size of which exceeds that of submicroscopic particles. Mercury porosimetry allows us to determine only pores ranging in size from 7.5 μm to 5.0 nm at pressures up to 150 MPa and to 3.75 nm at pressures up to 200 MPa (Table II).

The pore volume distribution as a function of pore radii is shown in Fig. 1. The curves allow one to infer that the copolymers do not contain pores above 500 nm. The pore radius of the highest frequency is 38 nm for the copolymer MMA–EDMA (polymer I) and 20 nm for the terpolymer HEMA–AN–EDMA (polymer IV). The pore distribution of the latter polymer is narrower (mean interval 5–36 nm compared with 3–73 nm), which means that the pores are more uniform. Differences with respect to the pore size distribution are not too pronounced, however. Both copolymers contain micropores, *i.e.*, pores smaller than 5 nm, because according to mercury porosimetry the pore distribution curves are not closed in the lower part. On the other hand, if one assumes a model pore distribution, the volume of micropores is comparatively small and does not vary too much for the copolymers taken for the comparison (0.014 cm^3/g for copolymer I and 0.020 cm^3/g for copolymer IV, Table II). A similar result is obtained for the pore volume from the capillary condensation of nitrogen, which allows one to characterize pores up to 35 nm.

The hysteresis of the porosimetric curve (Fig. 1) indicates the presence of “ink-bottle” shaped pores in macroporous copolymers, the content of which is considerable (23.6 and 18.7 vol.% relative to the total pore volume; 46 and 28 vol.% relative to the pore volume according to mercury porosimetry, retention factor $v_R = 0.46$ and 0.28)*.

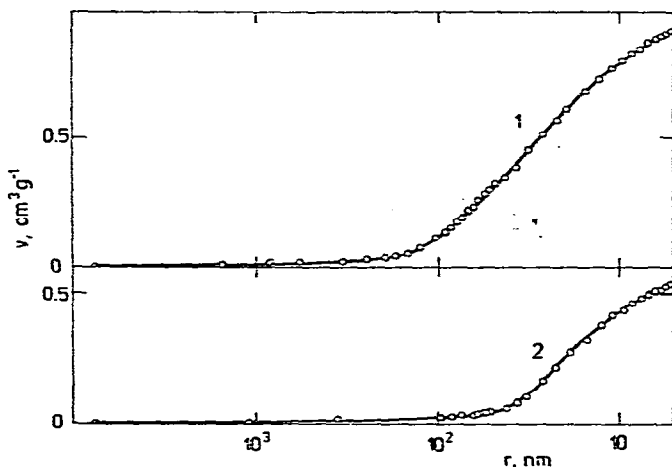


Fig. 1. Pore distribution of macroporous methacrylate copolymers by mercury porosimetry. 1, Polymer I; 2, polymer IV.

* The presence of “ink bottle” shaped pores in bead copolymers prepared by suspension copolymerization is also indirectly corroborated by the relatively low retention factor ($v_R = 0.11$) of Nuclepore¹¹ membranes having evidently cylinder-shaped pores which has been interpreted by the compressibility of the polymer.

Thus, the combination of methods described above may provide a general view of the porous structure. Differences in the porous structure of copolymers I and IV are predominantly due to the specific surface area (S_g : 196 and 57 m^2/g), specific pore volume (1.828 and 0.803 cm^3/g) and the different pore distributions.

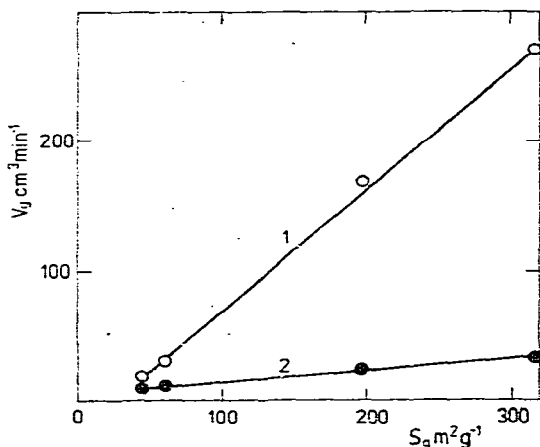


Fig. 2. Dependence of specific retention volumes of *n*-heptane (1) and ethanol (2) on the specific surface area of MMA-EDMA copolymers.

In the sorption and diffusion processes that occur during the retention of compounds injected on to macroporous copolymers, all of the properties of porous structure may become operative. The pore shape and distribution, *i.e.*, the fraction of micropores and "ink bottle" shaped pores, play their part together with the specific surface area. The retention time increases predominantly with increasing specific surface area of the sorbents (Fig. 2). The markedly lower specific retention volumes of hydrocarbons on copolymer IV compared with copolymers I-III (the values for which are lower than would correspond to the specific surface areas) are probably due to the lower content of the "ink-bottle" shaped pores of the former copolymer (0.51 cm^3/g compared with 0.431 cm^3/g). This is also suggested by the higher symmetry of peaks on this copolymer² and by the smaller dependence of the retention of heptane on the flow-rate at low flow-rates, argon (Fig. 3). Micropores also participate in the increase in retention¹², especially if one bears in mind that with

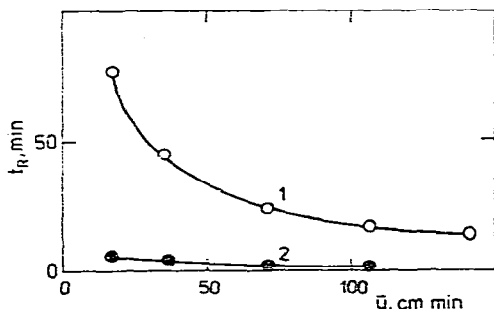


Fig. 3. Dependence of the retention time (t_R) of *n*-heptane on the linear flow-rate (\bar{u}) of carrier gas (argon). 1, Polymer I; 2, polymer IV.

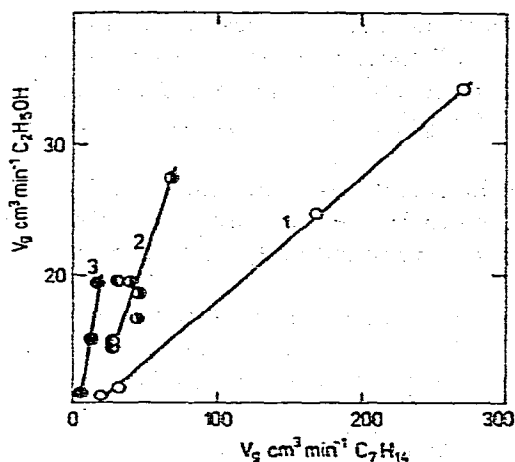


Fig. 4. Relationship between the specific retention volumes of ethanol and *n*-heptane on copolymers. (1) MMA-EDMA; (2) MMA-HEMA-EDMA; (3) HEMA-AN-EDMA.

respect to the globular structure of macroporous copolymers they also may be "ink bottle" shaped.

Whereas with HEMA and MMA copolymers the retention of *n*-heptane is considerably higher than that of ethanol, with AN copolymer the retentions of *n*-heptane and ethanol are similar, which indicates the high participation of specific interactions of the latter copolymer. The different participation of specific interactions in these three types of copolymers characterizes the dependence of the retention of ethanol on that of *n*-heptane for individual copolymers (Fig. 4). This relationship cannot be described adequately in terms of one dependence: each type of copolymer has its own. The cause is seen in the different enthalpies of sorption (ΔH_{CH_2}) of individual types of copolymers (Table III). The highest ΔH_{CH_2} values were established for MMA-EDMA copolymers (8.12–5.86 kJ/mole), which are close to those ascertained on graphitized carbon¹³. The ΔH_{CH_2} values of HEMA-MMA-EDMA terpolymers are slightly lower (6.99–5.94 kJ/mole), while those of the most polar HEMA-AN-EDMA copolymers (4.06–3.14 kJ/mole) are considerably lower. The differential enthalpies of sorption of the CH_2 group derived using a number of hydrocarbons and alcohols are approximately the same on non-polar copolymers, being

TABLE III
CHROMATOGRAPHIC PROPERTIES OF COPOLYMERS

Polymer	Specific retention volume, V_g (cm ³ /g)		Differential molar enthalpy of CH_2 group, ΔH_{CH_2} (kJ/mole)		Kováts retention indices				
	<i>n</i> -Heptane	Ethanol	Hydrocarbons	Alcohols	I_x	I_y	I_z	I_u	I_v
I	270	34.1	7.91	6.49	650	497	637	616	735
II	67.4	27.6	6.99	6.99	697	593	715	701	857
III	35.3	19.4	6.36	5.81	717	622	738	734	901
IV	15.0	11.0	4.06	4.02	910	877	968	1067	1259

higher for alkanes, whereas with polar copolymers the ΔH_{CH_2} values of alcohols and alkanes are close to each other; consequently, with these macroporous copolymers non-specific interactions predominate over specific interactions. The same view of the polarity of copolymers under investigation is suggested by the Kováts retention indices.

To summarize, therefore, differences in the retentions of alcohols and hydrocarbons on the given copolymers can be attributed to different enthalpies of sorption, while differences in the retentions of hydrocarbons on individual types of copolymers are due to their different porous structures.

Of practical importance is the finding that polar copolymers (AN copolymers) are particularly suitable for the separation of polar compounds. These copolymers can be used with advantage in analysis, because they allow one to analyse rapidly high-boiling compounds.

On the other hand, MMA copolymers, similarly to styrene-divinylbenzene copolymers, which in contrast to the AN copolymers possess a high specific surface area, are especially suitable for the analysis of volatile compounds and gases.

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