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REACTIVE POLYMERS

XXV*. MORPHOLOGY OF POLYMERIC SORBENTS BASED ON GLYCIDYL METHACRYLATE COPOLYMERS

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SUMMARY

Scanning electron microscopy was used to obtain basic data on the surface and internal morphology of macroporous copolymers based on glycidyl esters of methacrylic acid which are useful as chromatographic sorbents. The basic morphological units in beads consist of spherical microparticles (globules and nodules), hundredths to tenths of a micrometre in size. On the bead surface the globules are compactly arranged in the shell, owing to the surface tension in suspension copolymerization. The pores in the shell are an order of magnitude smaller than the macropores between the aggregates of globules inside the beads. With increasing content of the crosslinking agent in copolymers, the microparticles become finer and more individualized, which explains the increase in the specific surface area of the sorbents. In gas chromatography, the morphology of the sorbent preferentially determines the retention of non-polar compounds, while that of polar compounds is affected by the chemical composition of copolymers, that is, by the content of glycidyl epoxy groups in this instance.

INTRODUCTION

Polymeric sorbents are most frequently prepared by precipitation crosslinking copolymerization in which globular microparticles hundredths to tenths of a micrometre in size are formed[1]. The formation of a porous structure due to the aggregation of such microparticles was shown for the first time by electron microscopy using a copolymer of styrene and divinylbenzene[2,3]. The morphology and properties of the sorbent depend on the composition of the monomeric mixture and on the polymerization conditions, which determine the size of the microparticles and the character of their aggregation. Thus, for instance, with increasing content of the crosslinking

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agent a transition was observed from closed pores (4 % of the crosslinking agent) to a system of communicating pores between more isolated globules at 8 % of the crosslinking agent[4].

Little attention has so far been devoted to the investigation of the morphology of sorbents in gas chromatography. De Mets and Lagasse[5] and Sakodinskii and Panina[6] have published micrographs of sorbents of the styrene–divinylbenzene or ethylbenzene–divinylbenzene type without correlating the structure thus determined with the conditions of preparation or the chromatographic properties of the sorbents. Basic data on the morphology of styrene–divinylbenzene copolymers were given by Kun and Kunin[7], who investigated these copolymers as ion exchangers in their sulphonated or chloromethylated and aminated form. Differences in the surface morphology of the commercial sorbents Porapak Q, Chromosorb 101 and Chromosorb 102, as reflected in their chromatographic properties, have been described by Gearhart and Burke[8].

In earlier papers we characterized a number of polymeric sorbents based on glycidyl esters of methacrylic acid[9], and of the same copolymers modified by polymer-analogous reactions[10]. In this work we studied the surface and internal morphology of these copolymers using scanning electron microscopy (SEM) and correlated the results with their specific surface areas, chemical compositions and chromatographic properties.

EXPERIMENTAL

Preparation of copolymers

The sorbents were prepared by the suspension copolymerization of glycidyl methacrylate with ethylene dimethacrylate under conditions suitable for the formation of a macroporous structure. Inert components controlling the internal structure of copolymers were cyclohexanol and dodecanol in a volume ratio of 91:9. After completion of the reaction, the copolymers were freed from soluble components by decanting with water and methanol and by extraction with benzene and ethanol. They were then fractionated to the required grain size and dried in a vacuum drying box. In this way, a series of copolymers was obtained with the following composition (expressed as mass per cent of glycidyl methacrylate): sample No. 1, 3 %; No. 2, 21 %; No. 3, 44 %; No. 4, 55 %; and No. 5, 71 %.

Scanning electron microscopy

Particles of the copolymer samples were cut with a razor blade and fixed on a metallic support by using an adhesive polybutene layer. To remove interfering effects of the charge and to increase the emission of secondary electrons, the samples were coated with gold in a sputtering device (Balzers AG, Balzers, Liechtenstein). The micrographs were obtained with a JSM 35 scanning electron microscope (Jeol, Tokyo, Japan) in the secondary electron mode at an accelerating voltage of 15–25 kV. Micrographs with a higher resolution (below 10 nm) were obtained with a JEM 100B electron microscope using an ASID (Jeol) scanning adapter.

Gas chromatography

Packings with copolymers, bead size 150–200 μm, were conditioned prior to use by heating at 170° for 24 h in a stream of nitrogen at a flow-rate of 20 ml/min. The retention volumes of the sorbates were measured with a Pye apparatus (Pye Unicam, Cambridge, Great Britain) with straight glass columns (120 cm × 0.3 cm I.D.) at 150°, a flow-rate of argon of 25 ml/min and a dosage of 0.1 µl.

RESULTS AND DISCUSSION

As expected, the morphological investigation of glycidyl methacrylate copolymers revealed that their structure is globular. Cross-sections of the beads show an essential difference in the character of aggregation of the globules on the surface and inside the grains (Fig. 1). Microparticles on the surface and in the bulk are of the same size, but they are more compactly aggregated on the surface, owing to the compressive effect of the interfacial tension which operates in the suspension polymerization between the dispersed monomeric mixture and the aqueous phase. The surface shell of compactly aggregated globules forms some kind of vault, preventing the grain from contracting during the polymerization. The pores in the shell may be caused by the insufficiently close packing of globules during the polymerization, or additionally during the removal of low-molecular-weight components in the further treatment. The size of these pores in the shell (about 0.1 µm) is much smaller than that of communi-

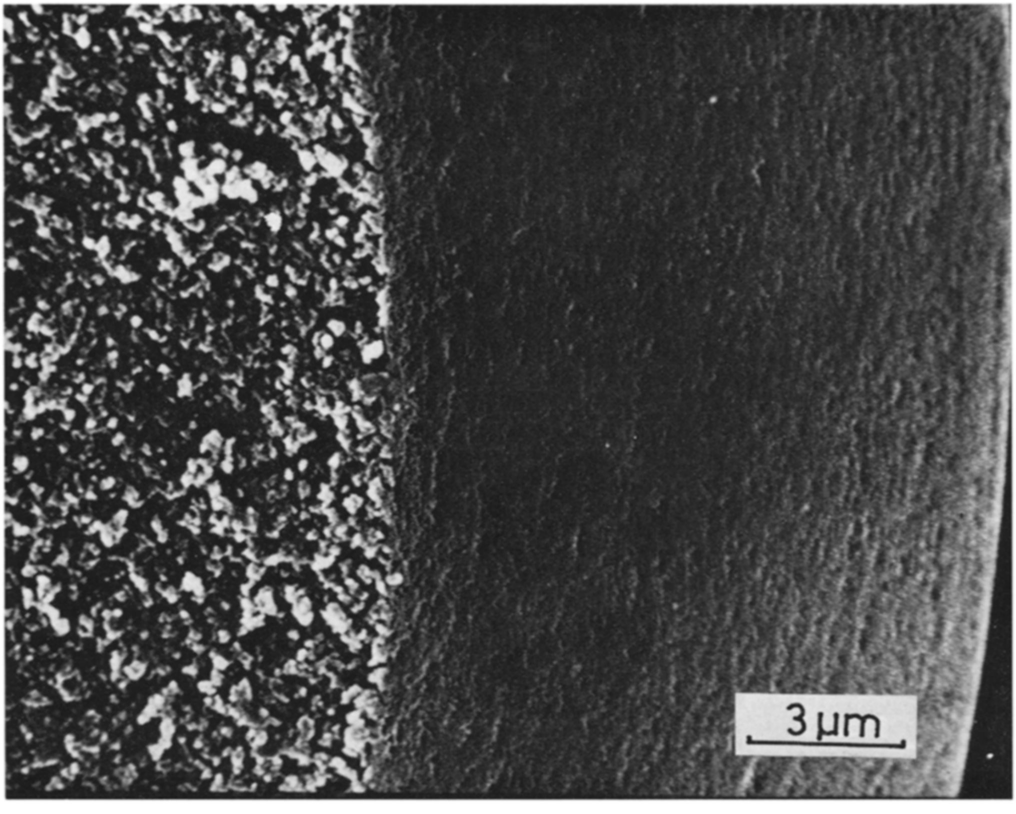

Fig. 1. Difference between surface and internal morphology (sample 2).

cating pores between aggregates of the globules inside the grain. Comparison of the character of the shell of variously crosslinked copolymers (Fig. 2) shows that the higher internal stress in the case of more crosslinked copolymers leads to creasing of the shell and to the formation of a larger amount of macropores.

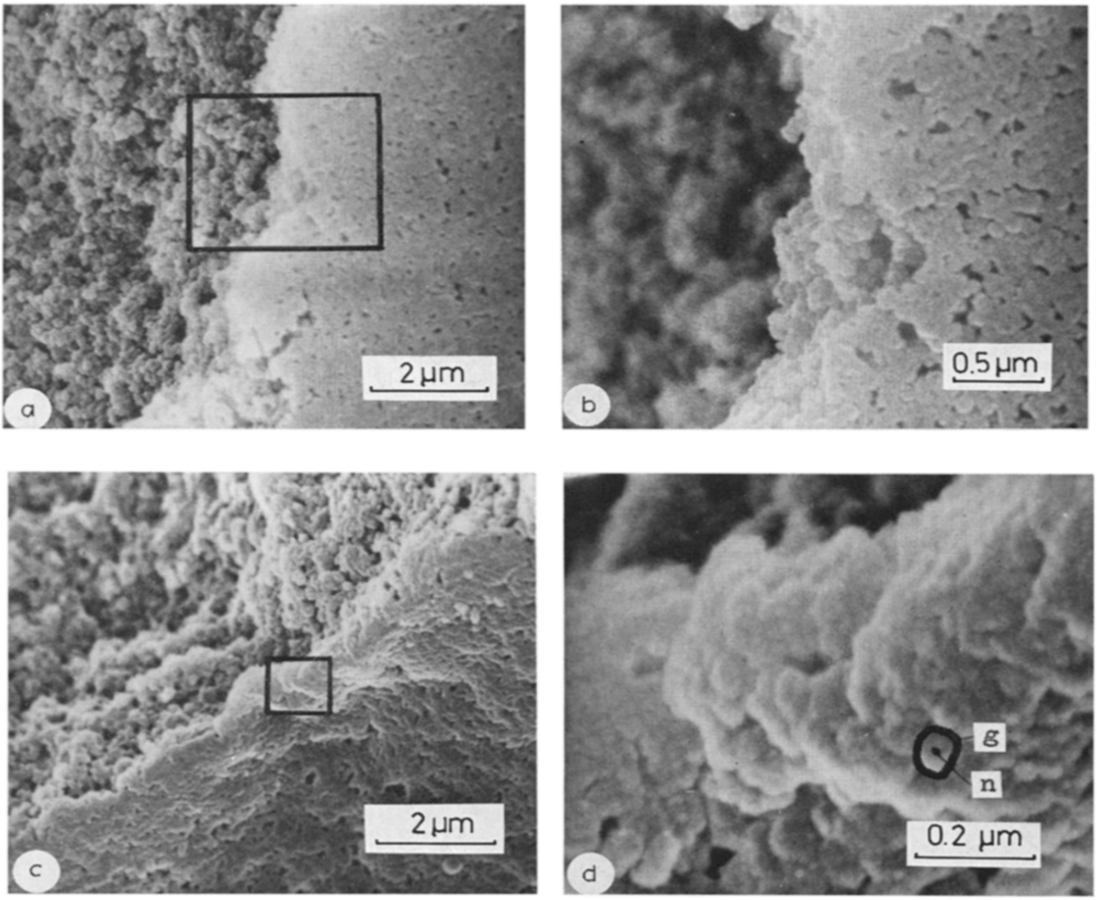

Fig. 2. Fine structure of copolymers with very different specific surface areas. (a) and (b), sample 5; (c) and (d), sample 1. (b) and (d), detailed micrographs of areas marked in (a) and (c), respectively.

The assumed mechanism of formation of a porous shell on the bead surface was confirmed by the study of the morphology of defective cavities, sporadically detected after cutting of some samples (Fig. 3). They are probably due to remaining traces of inert gas which was bubbled through the reaction mixture before the polymerization. The cavity surface consists of well distinguished, low-aggregated monodispersed globules (Fig. 3b). The non-compact packing of globules corroborates the above view of the compression effect of the interfacial tension, which in this instance (at the monomeric mixture–gas interface) is lower than in the formation of the surface shell at the monomeric mixture–water interface. Also, the high monodispersity of globules may be explained by a phenomenon which generally occurs during pre-

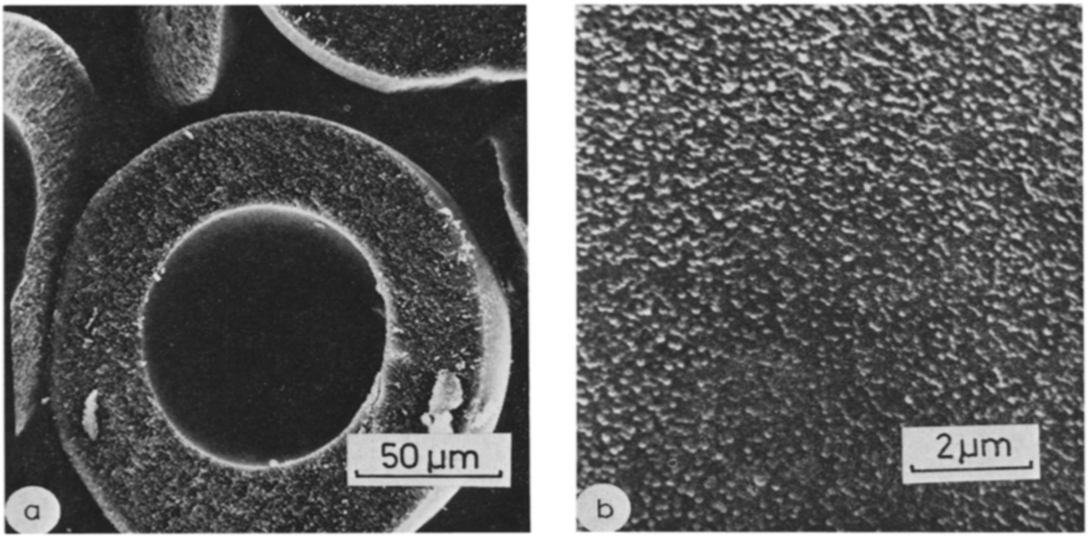

Fig. 3. (a) Defective cavity and (b) fine structure of the cavity surface.

cipitation polymerization: the globules suddenly separate at a certain conversion, their number quickly stabilizes and with proceeding polymerization only their size increases[1].

The size of globular particles and the character of their aggregation determine the specific surface area and porosity of the copolymers. As shown in Fig. 4, with increasing content of the crosslinking agent (ethylene dimethacrylate) the specific surface area of the sorbents also increases. At a higher content of the crosslinking agent, the phases separate faster while giving rise to smaller microparticles[1].

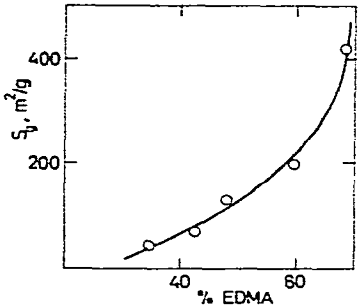

Fig. 4. Effect of the content of the crosslinking agent (EDMA) on the specific surface area (S_g) of copolymers (under otherwise identical conditions of preparation).

A good quantitative correlation was observed between the specific surface areas and sizes of microparticles. For a system of spherical, non-aggregating microparticles it holds that $S_g = 6/\varrho D$, where S_g (m^2/g) is the specific area, ϱ (g/cm^3) is the density of the polymer and D (μm) is the diameter of microparticles. At $\varrho = 1.2$ (g/cm^3), the sizes of microparticles according to calculations carried out with samples having very different surface areas (samples 1 and 5) should be 0.012 and 0.114 μm, respectively. A statistical evaluation of the mean diameters of microparticles from Fig. 2a and c yielded 0.065 ± 0.017 μm for sample 1 and 0.086 ± 0.021 μm for sample 5. As aggregation of microparticles reduces the surface area, its real values should be smaller than the calculated values. This is true for sample 5, but apparently not for sample 1. However, if the micrograph (Fig. 2d) of sample 1 (greatly magnified) is examined in greater detail, microparticles n (nodules) can be observed along with microparticles g (globules) actually measured; the size of these nodules is about 10 nm and explains adequately the large specific area of the sample concerned. All this indicates that, similarly to poly(vinyl chloride)[11], these copolymers also are composed of two types of microparticles, namely, primary ones called nodules, which aggregate to form secondary particles called globules. By analogy with the observed individualization of globules with increasing content of the crosslinking agent in copolymers of styrene and divinylbenzene[4], copolymers of GMA and EDMA exhibit individualization of nodules in the globules, which explains the pronounced increase in the specific surface area, especially at higher degrees of crosslinking.

The morphology of copolymers described above considerably influences their chromatographic properties. The increased roughness and porosity of the shell in the case of copolymers with a high content of the crosslinking agent (Fig. 2) may explain the relative decrease in the retention volumes observed with sample 1 (Fig. 5). In this instance, the shell forms a smaller barrier and has a considerable effect on the decrease in retention compared with the opposite effect of micropores, the content of which is higher in the sample with smaller microparticles. The relative retention volumes of non-polar sorbates (relative to pentane) increase, as expected, with increasing specific surface area or content of the crosslinking agent in copolymers (Table I). With polar sorbates, this effect of morphology is counteracted by the opposite effect of their chemical structure. Between the epoxy groups of glycidyl methacrylate units and molecules of polar sorbates there exist various strong specific interactions, so that in contrast, the relative retention volumes of these sorbates increase according to the

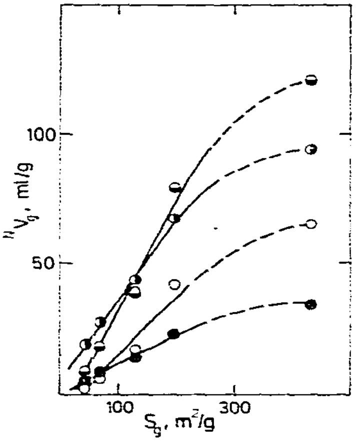

Fig. 5. Dependence of specific retention volumes (N_{V_g}) of *n*-hexane (○), ethanol (●), methyl ethyl ketone (◒) and nitromethane (◑) on specific surface areas (S_g) of glycidyl methacrylate copolymers.

TABLE I

RELATIVE RETENTION VOLUMES OF SORBATES ON THE COPOLYMERS UNDER INVESTIGATION

Measured at a column temperature of 150° and a flow-rate of argon of 25 ml/min; injection volume, 0.1 μl.

Sorbate	*Copolymer sample*				
	1	*2*	*3*	*4*	*5*
n-Pentane	1.00	1.00	1.00	1.00	1.00
n-Hexane	2.46	2.49	2.23	2.07	1.82
n-Heptane	6.35	6.26	4.97	4.07	2.91
n-Octane	—	15.71	11.44	7.89	4.64
n-Nonane	—	—	23.57	15.79	7.18
Methanol	0.57	0.66	1.03	1.89	4.36
Ethanol	1.30	1.37	1.82	3.14	4.64
Propanol	3.39	3.80	4.13	6.11	8.45
Butanol	9.42	9.40	9.71	12.25	13.09
Benzene	4.32	4.56	4.95	6.18	7.91
Methyl ethyl ketone	4.56	4.60	4.91	6.57	7.73
Nitromethane	3.54	4.02	5.45	9.93	17.91
Pyridine	—	—	13.34	20.39	25.09

extent of these interactions with increasing content of glycidyl methacrylate in the copolymer, or with decreasing content of the crosslinking agent. The relative retention volumes (Table I) indicate, together with the effect of the morphology of sorbents and of sorbent–sorbate interactions, also the effect of the boiling points (volatilities) of the individual sorbates.

The results seem to illustrate adequately the importance of a deeper insight into the morphology of polymeric sorbents in order to elucidate their chromatographic properties.

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