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REACTIVE POLYMERS

XL*. STUDY OF THE INTERNAL STRUCTURE OF THERMALLY TREATED POLYMERIC SORBENTS BASED ON GLYCIDYL METHACRYLATE COPOLYMERS

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SUMMARY

A decrease in the specific pore volume and specific surface area and an overall narrowing of the pore distribution are the main changes in the internal structure of thermally treated copolymers based on glycidyl methacrylate-ethylene dimethacrylate. They are also closely connected with changes in the chromatographic properties of polymeric sorbents thus treated. The decrease in the pore volume may be directly correlated with the decrease in the retention volumes.

INTRODUCTION

The chromatographic properties of macroporous polymeric sorbents are predominantly determined by their internal structure and chemical composition. The specific surface area and the specific pore volume or average pore radius are the characteristics most frequently used in the description of the internal structure of polymeric sorbents. In most instances, these data are obtained by the dynamic nitrogen desorption method¹⁻³. Some further valuable findings may be provided by electron microscopy⁴⁻⁶, which can show the globular order of microparticles and of their sizes. In addition, mercury porosimetry^{7,8} provides important information on the pore distribution at pore radii over 4 nm.

In a previous paper⁹ we described changes in the chromatographic properties of copolymers based on glycidyl methacrylate-ethylene dimethacrylate (GMA-EDMA) which had been exposed to brief heating, due to which some destruction had already taken place.

In this study we concentrated our attention on the internal structure of such thermally treated copolymers by combining mercury porosimetry and the sorption method based on capillary condensation of nitrogen. The data obtained were correlated with chromatographic results.

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EXPERIMENTAL

The thermal treatment of copolymers and conditions for the gas chromatographic measurement of the retention of sorbates have already been described⁹.

The specific pore volume was determined by the method of capillary condensation of nitrogen containing less than 1% of hydrogen using a Quantasorb apparatus (Quantachrome, Greenvale, NY, U.S.A.).

Porosimetric measurements

Prior to measurements, the copolymer samples were dried at room temperature and 0.6 kPa for 15 h. After being transferred into the measuring dilatometer, they were evacuated at 6 Pa for 1 h, then the dilatometer was filled with mercury at the same pressure. A Model 225 porosimeter (Carlo Erba, Milan, Italy) was used with a pressure range of $0-2 \cdot 10^5$ kPa, and an IBM 1370-135 computer was employed to process the results.

RESULTS AND DISCUSSION

The results of porosimetric measurements on thermally treated macroporous GMA-EDMA copolymers and the pore volumes determined by the method of capillary condensation of nitrogen are given in Table I. Differences in the V_p values obtained by the individual methods are due to the fact that the sorption method is suitable for pore radii between 1.5 and 30 nm, while mercury porosimetry records pores of radius 4 nm and greater. In both instances the cylindrical pore structure model was used. The V_p values obtained by mercury porosimetry are closer to reality, whereas the results of the sorption method detect the participation of micropores in the internal structure.

TABLE I

POROUS STRUCTURES OF INITIAL AND THERMALLY TREATED SAMPLES OF GLYCIDYL METHACRYLATE (GMA)-ETHYLENE DIMETHACRYLATE (EDMA) COPOLYMERS

Copolymer No.	Modification conditions		Mercury porosimetry*			Capillary condensation of N_2 *: V_p (cm^3/g)
	Temperature ($^{\circ}C$)	Time (h)	V_p (cm^3/g)	S_{Hg} (m^2/g)	$d/2$ (nm)	
1**	—	—	0.89	144	4-230	0.29
2	250	1	0.80	135	4-190	0.29
3	250	2	0.78	127	4-130	0.23
4	250	4	0.70	113	4-130	0.21
5	260	2	0.74	120	4-110	0.18
6	280	1	0.52	79	4-110	0.19
7***	—	—	1.22	194	4-200	0.31
8	250	1	0.76	99	4-120	0.21
9	250	2	0.63	64	5-120	0.18
10	260	2	0.50	58	5-80	0.09

* V_p = specific pore volume; S_{Hg} = specific surface area; $d/2$ = pore distribution.

** GMA:EDMA ratio in polymerization mixture = 45:55 (w/w).

*** GMA:EDMA ratio in polymerization mixture = 60:40 (w/w).

The results show that in both starting copolymers (samples 1 and 7) the thermal treatment leads to a decrease in the total pore volume. In agreement with earlier findings⁹, this decrease is more pronounced for the copolymer with the higher GMA content. If, for example, an identical depolymerization mechanism is assumed for both incorporated monomeric units, then the release of one GMA molecule is at least twice as likely as the release of the cross-linking agent that has reacted on both sides. This is why the copolymer richer in GMA is degraded more quickly. The specific surface area (Table I) were obtained by calculation from porosimetric measurements. Even though their accuracy is lower than that of data obtained by the sorption method⁹, it is obvious that the decrease in the specific surface area of thermally treated copolymers is in agreement with the decrease in the specific pore volume.

Morphological changes caused by the thermal treatment have the character of a sintering process and are reflected in the overall pore distribution. As demonstrated by Table I and Figs. 1 and 2, the upper boundary of the pore size decreases. This is due to the decrease in the particle volume caused by heating. Of the original 150–180 μm fraction, 30–50% of the particles have a diameter smaller than 150 μm , depending on the conditions of treatment¹⁰. It may be assumed that heating leads to sintering, and hence to the disappearance of micropores. This is suggested by the decrease in the V_p values measured by the sorption method and by the initial shape of the porosimetric curves of some of the thermally treated copolymers (predominantly in samples with a higher GMA content). Hence in the sintering process there is an overall narrowing of the pore distribution, which is a useful effect for the chromatographic sorbent. The results show that this narrowing of the pore distribution is affected by the sintering temperature rather than by the duration of thermal treatment (Figs. 1 and 2).

Table II demonstrates the main advantage of thermally treated GMA copolymers used as chromatographic sorbents, namely a reduction in retention times compared with the original sorbent. This, in turn, makes possible acceleration of the analysis or reduction of the working temperatures during the analysis. It can also be seen that the reduction in the retentions of non-polar hydrocarbons is greater than that of polar sorbates, in accordance with an earlier finding⁹ that the polarity of thermally treated GMA copolymers is higher than that of the original copolymers.

Correlation between the porosimetric and chromatographic data (Figs. 3 and 4) shows that there is a linear dependence between the decrease in the total pore volume of thermally treated copolymers and the reduction in the retentions on these samples. It should be pointed out, however, that deviations appear in the slopes of the straight lines obtained for copolymers with various contents of GMA. Under the same conditions of thermal treatment, the decrease in the pore volume of copolymer 1 is smaller (Fig. 3) than that of copolymer 7 (Fig. 4). The relatively larger decrease in the retentions of sorbates on sorbents derived from copolymer 1 may be explained through the fact that the internal structure of this less polar sorbent affects the retentions of compounds much more strongly. Hence, the decrease in the pore volume is also more markedly reflected in the retentions of both polar and non-polar sorbents. This is also indicated by the almost identical slopes of the straight lines for both hydrocarbons and polar sorbates (Fig. 3). In contrast, with the thermally treated and more polar copolymer 7, its chemical composition plays a more important role in the retention, which is also indicated by different slopes of the dependences for hydro-

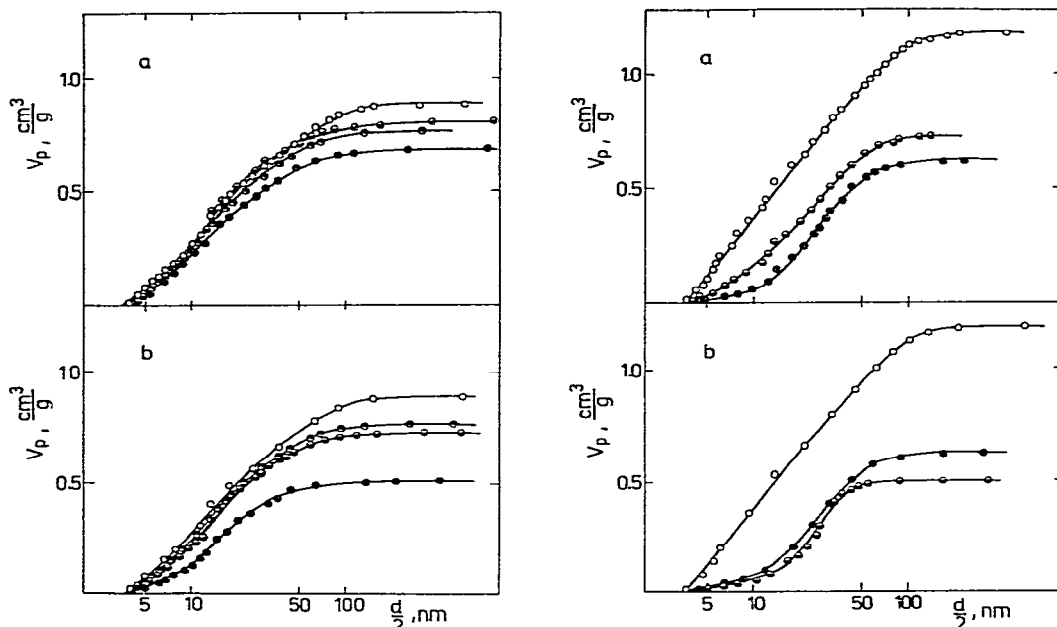


Fig. 1. Integral distribution curves of pore sizes of copolymers 1-6. (a) Effect of the time of thermal treatment: ○, copolymer 1 (original); ●, copolymer 2 (250°C, 1 h); ◐, copolymer 3 (250°C, 2 h); ●, copolymer 4 (250°C, 4 h). (b) Effect of temperature: ○, copolymer 1 (original); ◐, copolymer 3 (250°C, 2 h); ◑, copolymer 5 (260°C, 2 h); ●, copolymer 6 (280°C, 1 h).

Fig. 2. Integral distribution curves of pore sizes of copolymers 7-10 (a) Effect of the time of thermal treatment: ○, copolymer 7 (original); ◐, copolymer 8 (250°C, 1 h); ●, copolymer 9 (250°C, 2 h). (b) Effect of temperature: ○, copolymer 7 (original); ◑, copolymer 9 (250°C, 2 h); ◒, copolymer 10 (260°C, 2 h).

TABLE II

RELATIVE RETENTION VOLUMES OF SORBENTS ON THERMALLY TREATED SAMPLES OF COPOLYMERS RELATED TO THEIR RETENTION VOLUMES ON THE INITIAL COPOLYMER

Values determined at 150°C.

Sorbate	Copolymer No.									
	1	2	3	4	5	6	7	8	9	10
Pentane	1	0.48	0.32	0.35	0.44	0.22	1	0.58	0.50	0.38
Hexane	1	0.44	0.28	0.30	0.40	0.17	1	0.59	0.52	0.42
Heptane	1	0.39	0.24	0.27	0.36	0.14	1	0.55	0.47	0.41
Octane	1	0.34	0.19	0.20	0.32	0.10	1	0.50	0.43	0.37
Nonane	1	0.30	0.14	0.16	0.26	0.08	1	0.46	0.38	0.33
Benzene	1	0.52	0.44	0.47	0.56	0.34	1	0.78	0.73	0.70
2-Butanone	1	0.53	0.47	0.50	0.56	0.36	1	0.81	0.73	0.70
Nitromethane	1	0.89	0.75	0.83	0.82	0.69	1	0.99	0.97	0.96
Methanol	1	0.39	0.53	0.73	1.25	0.51	1	1.09	1.08	1.12
Ethanol	1	0.78	0.71	0.76	0.82	0.64	1	0.98	0.95	0.96
Propanol	1	0.69	0.62	0.63	0.70	0.49	1	0.89	0.85	0.83
Butanol	1	0.58	0.50	0.51	0.61	0.37	1	0.80	0.74	0.70

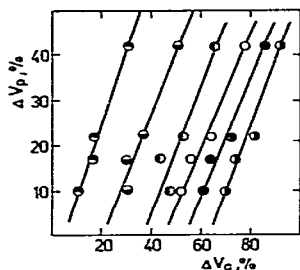


Fig. 3. Effect of decrease in the specific pore volume of samples obtained by the thermal treatment of copolymer 1 on the reduction of the retention volumes of sorbates; ○, pentane; ●, heptane; ●, nonane; ●, benzene; ○, propanol; ●, nitromethane.

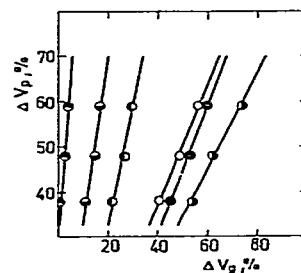


Fig. 4. Effect of decrease in the specific pore volume of samples obtained by the treatment of copolymer 7 on the reduction of the retention volumes of sorbates. Sorbates as in Fig. 3.

carbons and polar sorbates (Fig. 4). Similarly, the sintering effect affects the reduction of the retentions of non-polar compounds compared with the polar compounds.

The correlation between the chromatographic and porosimetric data indicates close relationships between changes in the internal structure and changes in the chromatographic properties of modified sorbents. The conclusions drawn from this study suggest further trends in controlling the structure of polymeric sorbents that possess optimal properties for practical chromatographic analyses.

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