Rearrangement of the porous structure of macroporous copolymers

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Changes in the porous structure of the strongly crosslinked macroporous copolymers glycidyl methacrylate–ethylene dimethacrylate and styrene–divinylbenzene were studied. Via interaction with organic solvents (dioxane, methanol) changes are brought about in the specific surface areas and pore volumes, which are interpreted in terms of changes in the microporous and macroporous domains of the porous structure of the polymers. According to mercury porosimetry, there are also changes in pore distribution. The phenomenon has also been observed in microphotographs of polymer sections obtained by electron microscopy and in the sorption of solutes.

(Keywords: porous structure; macroporous copolymers; porosimetry; crosslinking; methacrylate copolymers; styrene copolymers)

INTRODUCTION

As early as 1963 Millar and coworkers[1] described the preparation of the macroporous styrene–divinylbenzene (ST–DVB) copolymer and the criterion of macroporosity: uptake of cyclohexane greater than 0.1 ml g^{-1} and opalescence of beads. The conditions for the formation of a macroporous structure were reviewed in 1967 by Seidl *et al.*[2]. Since that time much work has been done regarding the influence of the diluent on the texture of a macroporous copolymer during copolymerization[3–5]. We have described changes in the porous structure of macroporous methacrylate copolymers during hydrolysis[6]. Such changes have also been observed with macroporous ST–DVB copolymers having low specific surface area[7] values after consecutive chemical transformations[8–11] of macroporous methacrylate and bead cellulose[12], and with chromatographic sorbents[13]. In these cases, mainly copolymers crosslinked to a lower degree were involved, in which changes in swelling were observed to depend on the solvent used. Macroporous copolymers crosslinked to a high degree, in which such changes are almost imperceptible, have so far been regarded as completely rigid systems. We were therefore interested to find out whether changes in the porous structure also occur in such strongly crosslinked systems.

EXPERIMENTAL

Copolymers used

The copolymers used were as follows. G5 and G60 are suspension copolymers of glycidyl methacrylate with ethylene dimethacrylate (95 and 40 wt%)[14]. Synachrom E5 is a copolymer of styrene and divinylbenzene (Labora, Brno). Amberlite XAD-2 and XAD-4 are copolymers of styrene with divinylbenzene (Rohm and Haas, Philadelphia).

Modification of the porous structure

The polymer was washed with dioxane and left to stand for 24 h. Then it was washed with a fivefold amount of methanol and diethyl ether, and dried at room temperature under a vacuum of 1.3 kPa.

Methods

Mercury porosimetry of polymer samples was carried out using a Carlo Erba Strumentazione Milano model 2000 apparatus. Specific surface area was determined by the low temperature adsorption of nitrogen using the three-point Brunauer–Emmett–Teller (BET) method. Pore volume was determined from cyclohexane regain by employing the centrifugation technique.

Microphotographs of particle fractures were obtained by means of a scanning electron microscope JSM 35 (JEOL). From SEM micrographs of the original fractures and by drying modified samples from various swelling agents, statistical mean dimensions of agglomerates of particles, isotropic pores between globules in agglomerates and anisotropic cracks between agglomerates were determined (in the latter case, the crack width was measured).

Sorption measurements

The copolymers were packed into glass columns (9 cm × 0.3 cm i.d.). Measurements were carried out using a chromatograph equipped with flame ionization detection (f.i.d.) at a nitrogen flow rate of 40 ml min^{-1} and column temperature of 100°C. For chromatographic

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Table 1 Treatment of the porous structure of macroporous copolymers by a physical procedure (S_g = specific surface area; V_g = specific volume)

Copolymer	Composition	Crosslinking agent	S_g (m^2 g^{-1})		V_g (ml g^{-1})	
			a	*b*	*c*	*b*
G60	GMA–EDMA	40	51.9	110	0.974	0.927
G60[d]	GMA–EDMA	40	58.5	171	1.385	1.117
G5	GMA–EDMA	95	367	149	0.807	1.228
G5[d]	GMA–EDMA	95	285	176	1.215	1.823
Synachrom E5	ST–DVB	27	133	178	2.075	2.225
Synachrom E5[d]	ST–DVB	27	395	127	2.030	1.218
Amberlite XAD-2	ST–DVB	27	196	89	0.128	0.550
Amberlite XAD-2[d]	ST–DVB	27	302	125	0.460	0.668
Amberlite XAD-4	DVB	54	690	147	1.252	0.791
Amberlite XAD-4[d]	DVB	54	659	116	1.227	0.735

[a] According to the thermal desorption of nitrogen
[b] According to mercury porosimetry
[c] According to cyclohexane regain
[d] Polymer with modified porous structure

standards, hexane, ethanol, amyl alcohol and pyridine were used, and their specific retention volumes (V_g, ml g^{-1}) were determined.

Sorption of surface-active compounds (Triton X-100, X-305 and X-405) from water by macroporous copolymers G5 has been determined spectrophotometrically. The values of the maxima of the sorption isotherms are shown later in *Table 4*.

RESULTS

As can be seen in *Table 1* and *Figures 1* and 2, the interaction of macroporous copolymers with a solvent (dioxane) and drying at reduced pressure and room temperature cause changes in the porous structure, characterized by the specific surface area, pore volume and pore distribution. The greatest changes arise in the specific surface area values determined by the three-point BET method, which reflect changes in the microporous domain.

In most cases the fraction of micropores increases; only in those pores that have a developed microporous structure (G5 and Amberlite XAD-4) can a partial loss of micropores be observed.

In contrast, the pore volume values are sensitive to the fraction of macropores and not sensitive to small pores. With some exceptions only (Amberlite XAD-2), the pore volume values determined from cyclohexane retention are comparable with values obtained by mercury porosimetry.

As can be seen in *Figures 1* and *2*, the greatest changes due to the action of solvents take place in methacrylate copolymers G5 and G60, where the pore volume increases and in the case of G5 becomes double the original value. The increasing pore volume values after swelling in dioxane suggest that, in most cases, the macroporous fraction increases.

The number distribution function derived assuming a

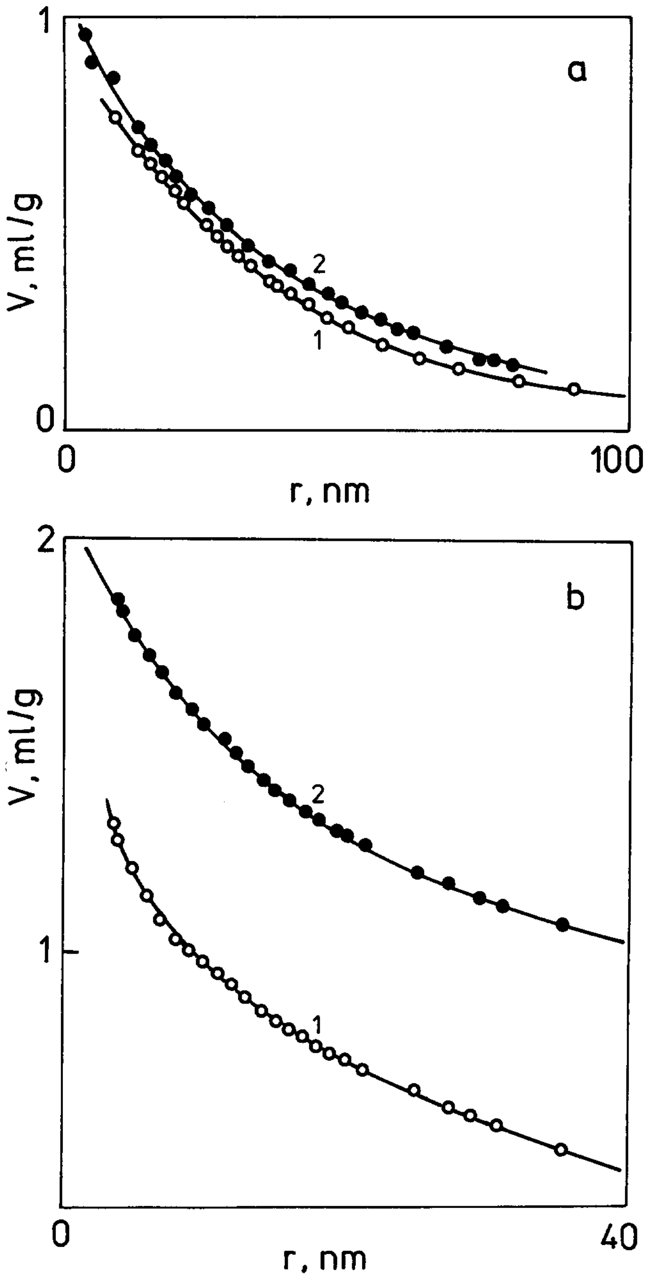

Figure 1 Dependence of pore volume on the pore size of methacrylate macroporous copolymers G60 (a) and G5 (b): curve 1, starting copolymer; curve 2, after treatment with solvents

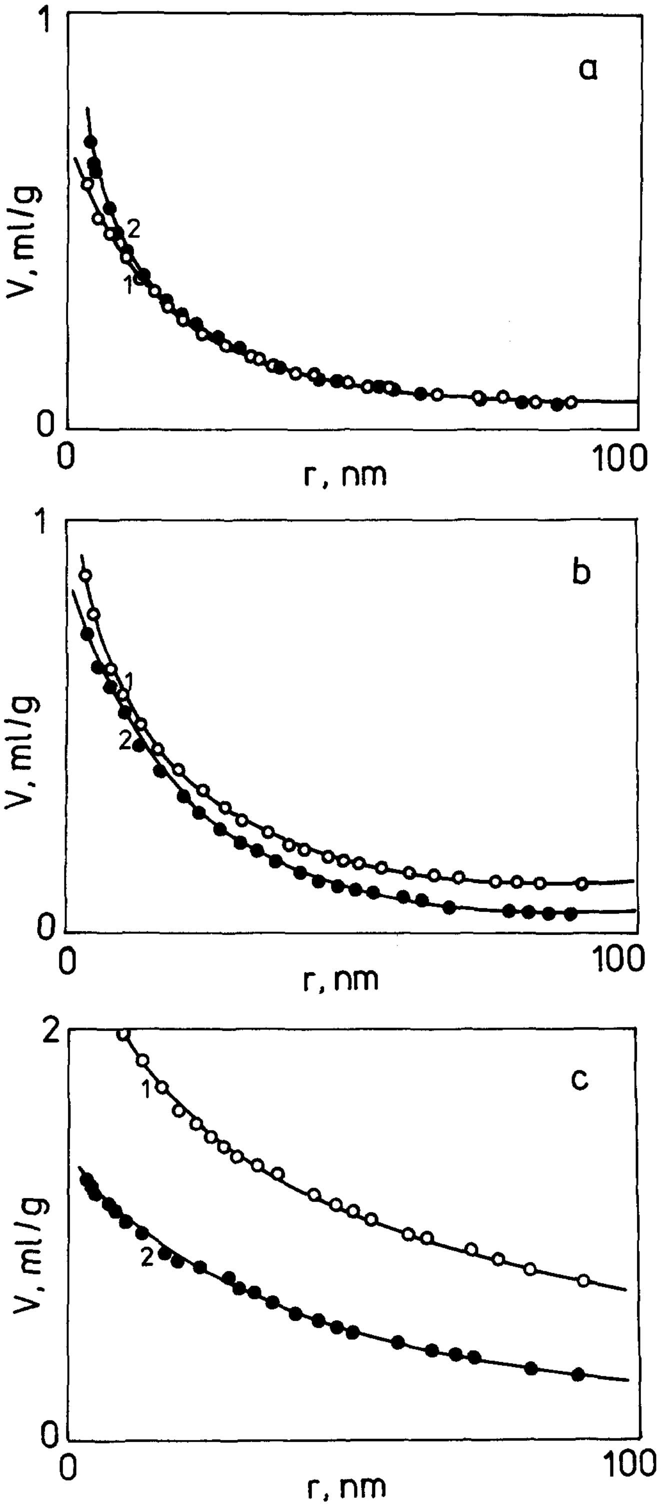

Figure 2 Dependence of pore volume on the pore size of macroporous ST–DVB copolymers Amberlite XAD-2 (a), XAD-4 (b) and Synachrom E5 (c): curve 1, starting copolymer; curve 2, after treatment with solvents

spherical model of the porous structure, that is:

$$f(r_N) = \frac{3v}{4\pi r^3} \qquad (1)$$

has a uniform shape for all the polymers under study, with a peak at 3.7 nm, i.e. beyond the measurable region. However, the volume distribution function:

$$f(v_V) = \frac{v}{\log(r)} \qquad f(r_V) = \frac{\mathrm{d}v}{\mathrm{d}r} \qquad (2)$$

always has further maxima in the measured region. Most of the volume distribution functions (*Figures 3* and *4*) have a decreasing character in the interval between 3.74 and 300 nm, and the peaks are situated in the range 4–15 nm and 150 nm. On interacting with a solvent, one can see a slight displacement of the dependence towards micropores and unification of distribution ensuing from a decrease in the frequency function values. The closeness of the curves for the original and modified dependences suggests an absolute error of 0.005–0.01 units in the frequency function ($v/\log(r)$), which corresponds to a relative error between 7 and 14%. Hence, the peaks observed are statistically significant.

Peaks in the microporous region also confirm values of the mean pore radii calculated from the specific surface areas and pore volumes (*Table 2*) by using the equation:

$$r = 2000 V_g / S_g \quad \text{(nm)} \qquad (3)$$

The most pronounced changes have been observed with Synachrom E5 in the macroporous region, while changes in copolymers crosslinked to a high degree were unpronounced (Amberlite XAD-4, G5).

The texture of macroporous copolymers prepared by radical suspension polymerization consists of microspheres (diameter 50–100 nm) formed around elementary nuclei (10–20 nm). Microsphere aggregates (250–500 nm) are separated by large pores; there are smaller pores (<4 nm) in the microspheres between the nuclei and

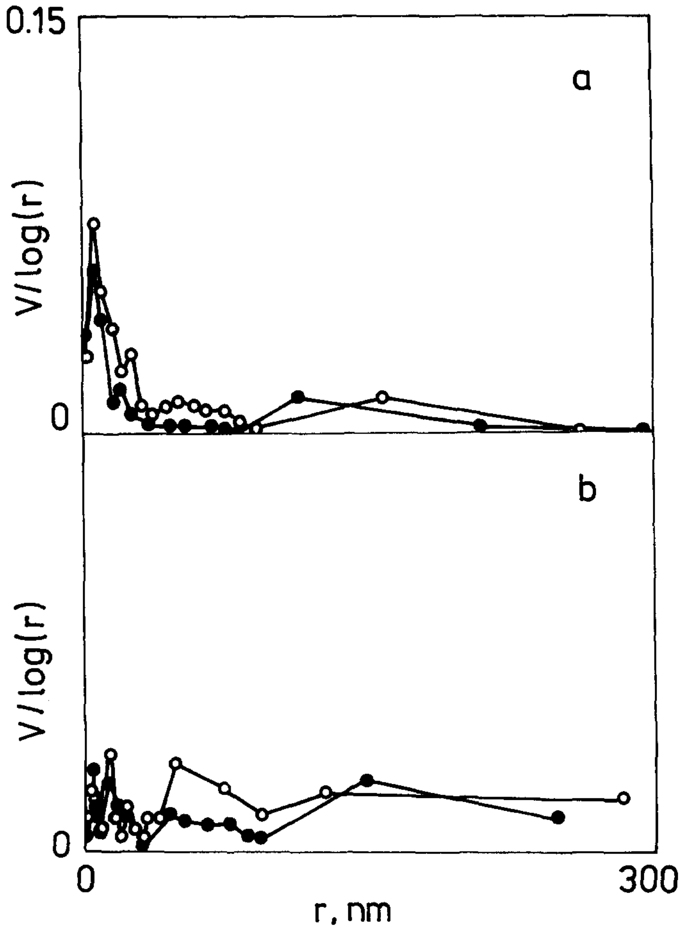

Figure 3 Pore distribution in macroporous methacrylate copolymers G60 (a) and G5 (b): curve 1, starting copolymer; curve 2, after treatment with solvents

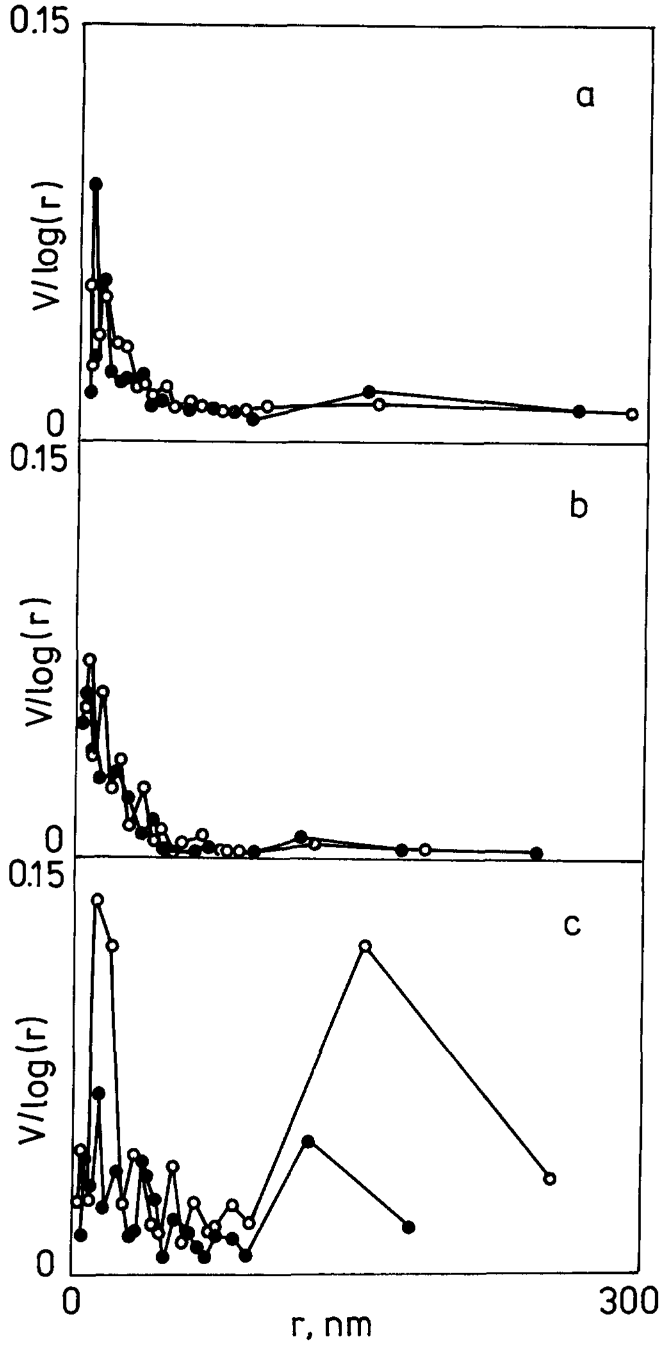

Figure 4 Pore distribution of macroporous copolymers Amberlite XAD-2 (a), XAD-4 (b) and Synachrom E5 (c): curve 1, starting copolymer; curve 2 after treatment with solvents

intermediate pores (transitional pores or mesopores, 4–50 nm) in the aggregates between the microspheres; the large pores range[5] from 50 nm to more than 1000 nm.

Changes in the porous structure can also be observed in microphotographs obtained in an electron microscope (*Figures 5* and *6*). The sizes of nodules and micropores are below the resolution of the microscope used. The porous structure of macroporous copolymers consists of comparatively irregular globules and their aggregates. Along with micropores (<2.5 nm), cracks between the aggregates that form macropores (>50 nm) also appear between the globules.

Globules of the copolymer G5 (*Figure 5*) and the pore size are approximately the same. After modification, the pores increase, and a partial agglomeration of the particles takes place.

The copolymer G60 (*Figure 5*) consists of globules of approximately the same size, but their agglomerates are larger (1400 nm) than those in the case of G5. Microparticles are only a little larger compared with G5, while the agglomerates are noticeably larger.

The changes occurring in methacrylate copolymers due to solvents are not too great, and are reflected in morphology predominantly in crack formation. The greatest changes have been observed after the modification of ST–DVB copolymers (Synachrom E5, Amberlite XAD-2) (*Figure 6*). Microparticles aggregated following modification, and cracks appeared (500–1000 nm). Amberlite XAD-4, a copolymer of technical DVB (position isomers DVB, EVB (ethylvinylbenzene) and ST), has a porous structure consisting of aggregated microparticles. The effect of the solvent causes a distinct separation of the aggregated globules.

Further evidence about changes in the porous structure after reswelling is provided by sorption measurements of standards in the gas and liquid phases. As follows from *Table 3*, sorption of non-polar (hexane) and polar

Table 2 Pore sizes of macroporous copolymers treated by a physical procedure

	Mean porous radius (nm)		
		b	
Copolymer	*a*	First maximum	Second maximum
G60	37.5	116	
G60[c]	47.3	133	
G5	4.4	103	2814
G5[c]	8.5	49	2389
Synachrom E5	31.2	66	2831
Synachrom E5[c]	10.3	143	3159
Amberlite XAD-2	1.3	43	
Amberlite XAD-2[c]	3.05	43	
Amberlite XAD-4	3.6	37.4	
Amberlite XAD-4[c]	3.7	69	

[a] Calculated from sorption data and cyclohexane regain
[b] Peaks of pore distribution determined by mercury porosimetry
[c] Polymer with modified structure

Table 3 Specific retention volume V_g (ml g^{-1}) of solutes on methacrylate macroporous copolymers at 100°C

Copolymer	Hexane	Ethanol	Pyridine	Amyl alcohol
G5	875	286	2561	
G5[a]	354	352		
G5[b]	143		420	499
G5[a,b]	189	67	522	801
Synachrom E5	220	83	1115	823
Synachrom E5[a]	614	156	2560	3443
Amberlite XAD-2	182	52	456	651
Amberlite XAD-2[a]	314	47	523	657
Amberlite XAD-4	864	95	1286	
Amberlite XAD-4[a]	958	106	1292	

[a] Polymer with modified porous structure
[b] At 150°C

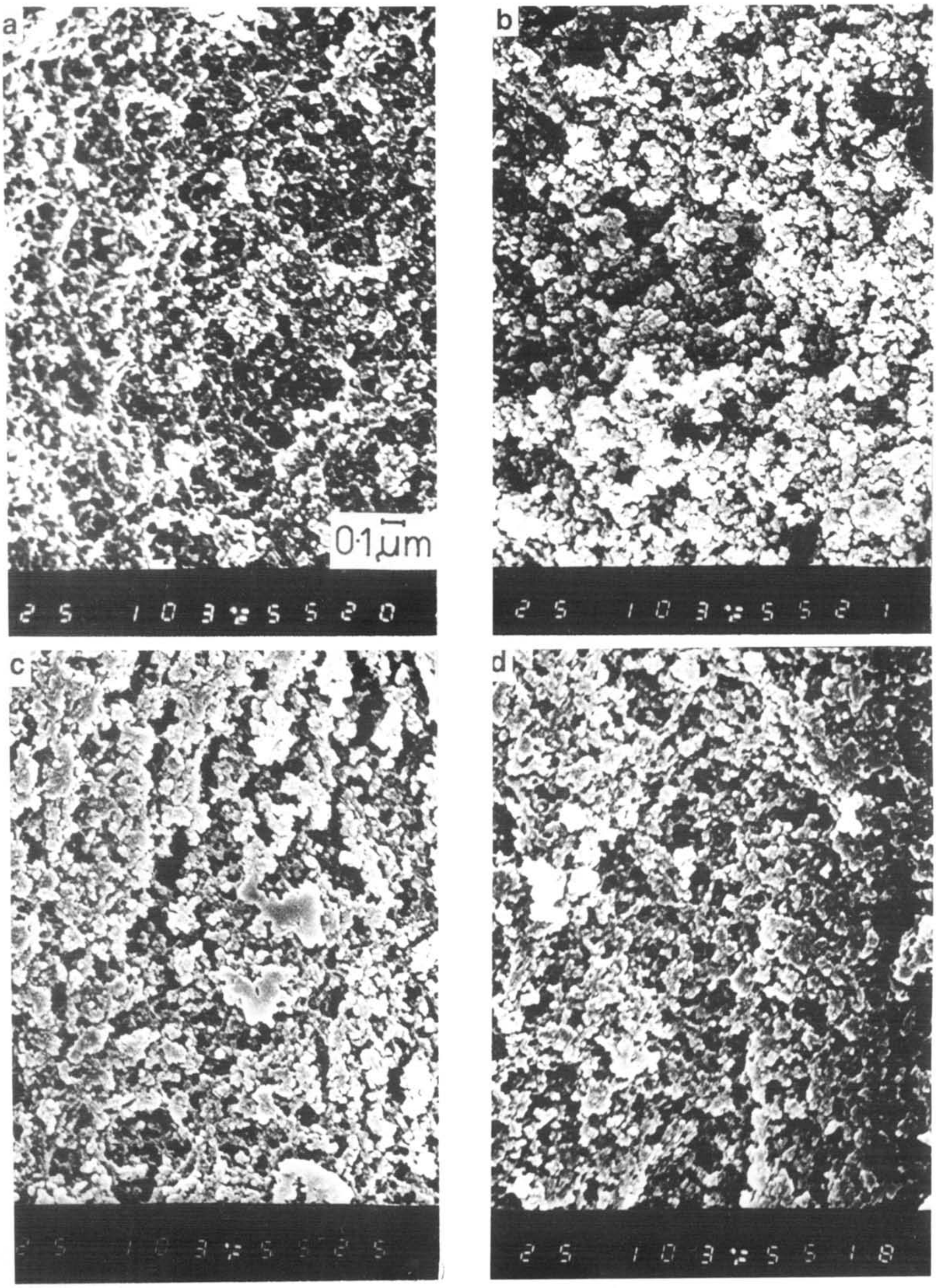

Figure 5 Microphotographs of macroporous copolymers G60 (a, b) and G5 (c, d) before treatment (a, c) and after swelling in dioxane, transfer into methanol and drying at room temperature *in vacuo* (b, d)

solvents (ethanol, amyl alcohol and pyridine) is always higher onto sorbents after solvent treatment in comparison with untreated ones. The same results are observed in the sorption of surface-active compounds (oligooxyethylene benzenes) by the sorbents under investigation. As follows from *Table 4* the sorbent with physically modified structure sorbed twice the amount of the surface-active compound compared with the unmodified starting copolymer[15].

Table 4 Sorption of surface-active compounds by methacrylate copolymer G5[15]

	Triton (mmol g^{-1})		
Sorbent	X-100	X-305	X-405
G5	0.31	0.30	0.22
G5[a]	0.60	0.74	0.32

[a] Polymer with modified porous structure

DISCUSSION

Macroporous copolymers based on styrene, methacrylates or acrylates are used especially in sorption and separation processes or in catalysis. The processes involved are those where diffusion of the compound (sorbate) into the bulk of the polymer (sorbent) affects the final result of the operation. By facilitating the accessibility of the sorbent to molecules of a low or high mass selectivity, the effectiveness of the above operations can be increased. The porous structure of macroporous copolymers based on styrene, alkyl methacrylates or acrylates can be

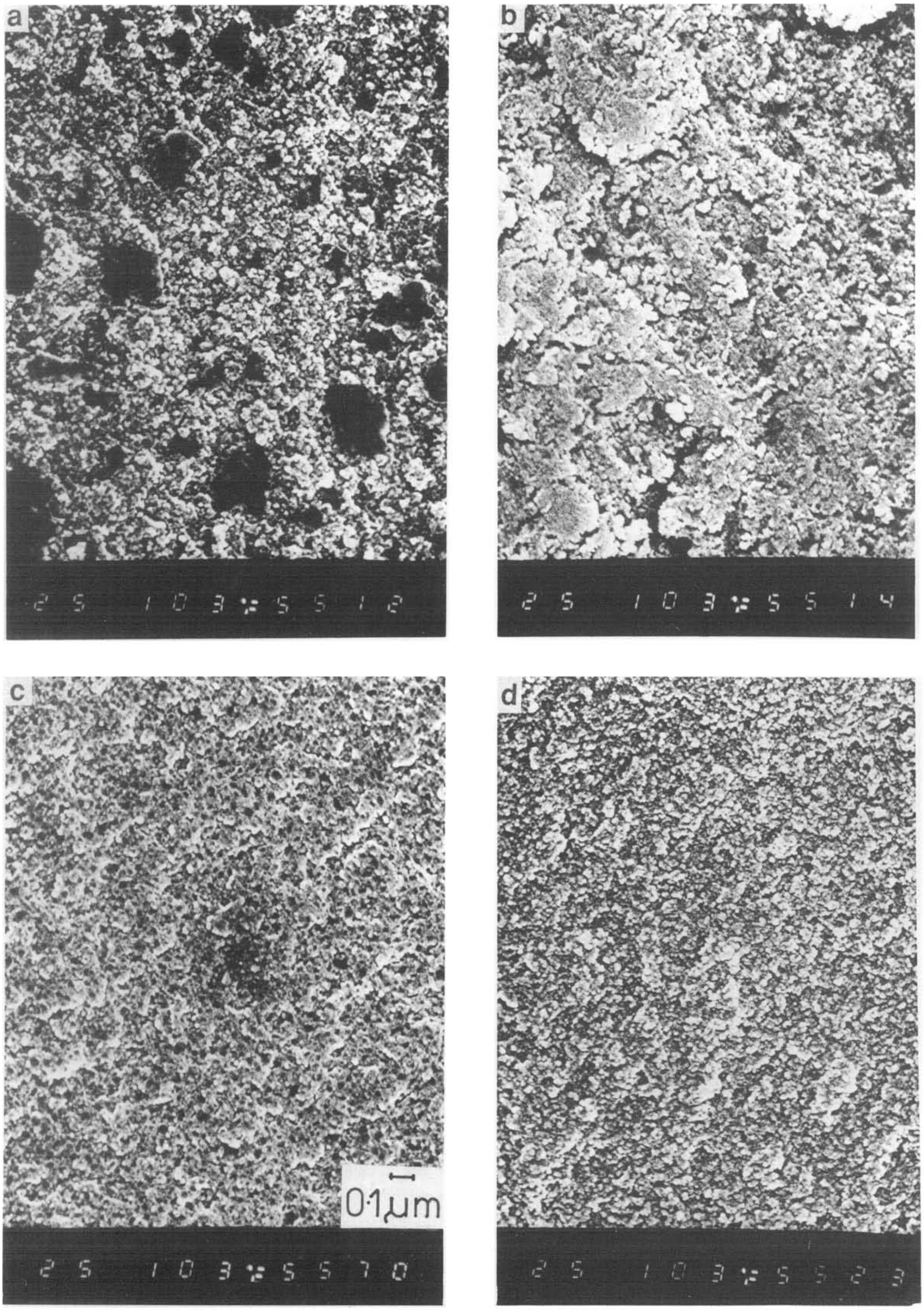

Figure 6 Microphotographs of macroporous copolymers Amberlite XAD-2 (a, b), XAD-4 (c, d) and Synachrom E5 (e, f) before treatment (a, c, e) and after swelling in dioxane, transfer into methanol and drying at room temperature *in vacuo* (b, d, f)

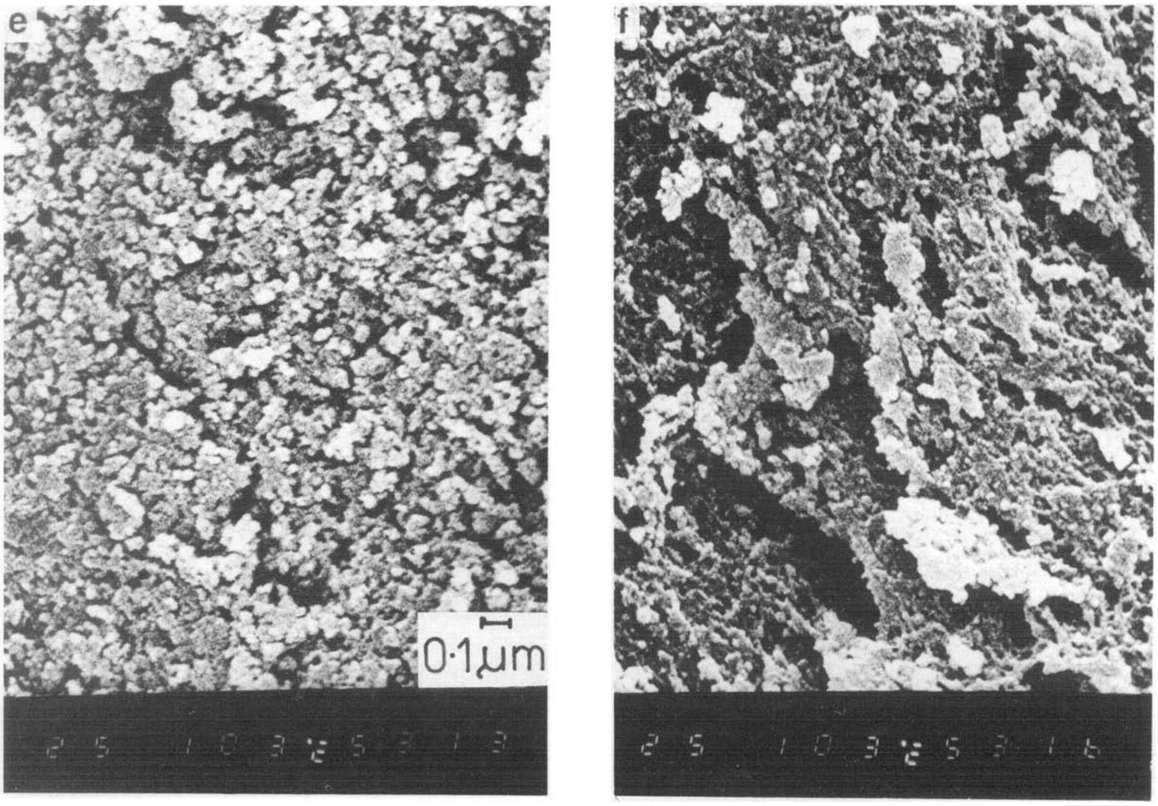

Figure 6 *Continued*

adjusted by consecutive interaction with solvents and by regulation of the drying processes. Thus, for example by drying from a thermodynamically good solvent and at temperatures above T_g of the polymer, porosity decreases and the pore size increases. On the contrary, a step-by-step transfer into a thermodynamically poor solvent and drying at temperatures below T_g cause an increase in polymer porosity and a decrease in pore size.

Major changes brought about by the interaction of dioxane with methacrylate copolymers ensue from the lower T_g of these copolymers[16] compared with ST–DVB (40°C compared with 110°C) and from the fact that for methacrylate copolymers dioxane is a thermodynamically good solvent.

The stability of the porous structure was also investigated in the case of copolymers of EVB with DVB[17] and changes were observed in the retention of ethanol and toluene up to 54% DVB. Similarly, Takeda *et al.*[18] investigated crosslinked polystyrenes by mercury porosimetry. Also, it was found that pores are opened by use of good solvents (e.g. if methanol, a poor solvent, is replaced with 1,2-dichloroethane) or by heating above the T_g of the polymer. Unlike macroporous copolymers, crosslinked polystyrenes swell more, and this has been interpreted as the 'shape memory' of the polymer due to the linking of crosslinked sites by chains of the microgel.

The nature of the process consists of the fact that strongly crosslinked copolymers also swell in good solvents (i.e. those with a low Flory interaction parameter χ), though to a limited extent only. The solvents are 1,2-dichloroethane ($\chi = 0.4$ for the ST–DVB copolymer), dioxane and the like. Drying from such solvents, especially at temperatures above the glass transition temperature of the polymer, causes sintering of the globules, which represent the main morphological formation of the polymer structure, thus leading to a decrease in porosity and micropores and an increase in the fraction of macropores. Drying at temperatures below T_g (at reduced pressure) from thermodynamically poor solvents allows both porosity and micropores of the system to be preserved to a great extent.

The adhesive power of swollen globules and of the microgel that is usually present also cannot be neglected. This only supports sintering of the microparticles.

Gradual transfer of the polymer from a good solvent into a poor one, which may be carried out owing to the miscibility of the solvents used through solvents miscible with both the good and the poor solvents, leads to deswelling and separation of submicroparticles, and thus also to an increase in porosity and in the fraction of micropores. Poor solvents are, for example, diethyl ether and methanol ($\chi = 1.7$ for ST–DVB copolymer). By reswelling in a good solvent, dry polymers with an inadequate porosity and pore size can be transformed into a state where further choice of solvent and of the drying procedure would lead to a product possessing the required properties.

As follows from *Tables 3* and *4*, solvent-modified sorbents had better sorption properties.

CONCLUSIONS

The porous structure of highly crosslinked copolymers is not rigid at all. By interacting with organic solvents, changes occur in the specific surface areas, pore volumes and sorption properties, which are interpreted as due to changes in the microporous and macroporous domains of the porous structure of the polymers. The solvent treatment described allows us to increase the sorption of commercial polymers, which are usually not dried under optimal conditions.

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