INVESTIGATION OF THE SURFACE STRUCTURE OF POLYMERS BY CHROMATOGRAPHIC METHODS

V. USE OF GEL PERMEATION CHROMATOGRAPHY IN THE STUDY OF THE POROUS STRUCTURE OF COPOLYMERS OF GLYCIDYL METHACRYLATE

J. HRADIL*, D. HORÁK, Z. PELZBAUER, E. VOTAVOVÁ, F. ŠVEC and J. KÁLAL

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6 (Czechoslovakia)

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SUMMARY

Gel permeation chromatography (GPC) was used in an inversion function to characterize the porous structure of macroporous copolymers. Using macroporous glycidyl methacrylate copolymers as an example, the relationships between the exclusion limit in GPC and the pore size and porosity of the sorbent, the distribution coefficient and the pore geometry and size, and the peak widening and morphology of the porous structure were established. Characteristic quantities are compared with results provided by other methods, especially electron microscopy, mercury porosimetry and nitrogen sorption. It was demonstrated that the porous structures of strongly cross-linked macroporous copolymers in the swollen and dry states differ.

INTRODUCTION

There are a number of methods which can be used in the investigation of the porous structure of sorbents, but most of them require measurements in the dry state. Whereas for rigid inorganic sorbents these data also hold in the liquid, with polymers the properties of the porous structure may differ after drying owing to swelling of the polymers or to differences in wetting. For this reason, a search for methods allowing the characterization of porous polymers in the liquid state is called for. Gel permeation chromatography (GPC) is suitable for this purpose if applied inversely, *i.e.*, in the characterization of the porous structure of the copolymer.

The inverse procedure for the investigation of polymers often used in gas chromatography is not common in gel permeation chromatography[1]. Whereas by using gas chromatography a number of properties may be determined that are related to the chemical structure of the phase under study, gel chromatography is expected to supply information on the supermolecular structure, *i.e.*, morphology of polymer

sorbents. The method in which penetration of large dye molecules into the porous structure is applied was one of the first used in the pore size determination[2].

In this study we tried to establish the possibilities offered by gel permeation chromatography in the characterization of porous polymeric materials and to provide a critical evaluation of the particular methods.

EXPERIMENTAL

Materials

Macroporous glycidyl methacrylate–co-ethylene dimethacrylate copolymers (32.5 mass-% of cross-linking agent) were prepared by radical polymerization[3,4] in the presence of various types [poly(vinyl alcohol), poly(vinylpyrrolidone)] and contents (0.007–2.5 wt.-%) of the suspension stabilizer using 1-dodecanol and cyclohexanol as porogenic diluents (Table I). A turbine was used in the preparation of samples 1 and 2 and an anchor stirrer in that of sample 3. A fraction sieved through a sieve smaller than 0.1 mm was used with sample 1, and a fraction of size 25–60 μm with an Alpine MZR 100 apparatus with samples 2 and 3.

TABLE I

CHARACTERIZATION OF SORBENTS

Composition of the polymerization mixture was the same in all instances. Volume ratio of continuous to dispersed phase = 3:1, monomers to inert components = 2:3, glycidyl methacrylate to ethylene dimethacrylate = 2.1:1, 1-dodecanol to cyclohexanol = 1:9; 0.5% (w/w) 2,2'-azobisisobutyronitrile.

| Sample | Suspension stabilizer | | Interfacial tension of continuous and dispersed phases (mN m^{-1}) | Mean radius (μm) |
	Type	Concentration (%, w/w)		
1	Poly(vinyl alcohol)	0.007	75	729
2	Polyvinylpyrrolidone K90	2.5	41	28
3	Poly(vinyl alcohol)	2.0	18	35

Methods

The columns (120 × 0.8 cm I.D.) were packed with sorbents under pressure by a floating procedure. Various standards, such as polydextrans, saccharose, methanol, poly(ethylene glycol), triethylene glycol and diethylene glycol, were injected in an amount of 3.2 cm^3 of 0.1% solution at a flow-rate 40 cm^3 h^{-1} of distilled water (2.5–150 cm^3 h^{-1} while observing the widening of the peaks). The elution volumes thus obtained were used to determine the upper and lower exclusion limits of copolymers, distribution coefficients and accessible porosity.

The specific surface area of the sorbents was determined by using the dynamic nitrogen desorption method, the pore distribution was determined at various nitrogen to hydrogen ratios in the range 1.6–44 nm and the pore volume was assessed from the cyclohexane or water regain by the centrifugation technique.

Micrographs of the porous structure of the sorbents were obtained with a JSM 35 scanning electron microscope with an accelerating voltage of 25 kV. Sorbent grains

were cut with a razor blade, fixed on to the support with adhesive and, for providing surface conductivity, coated with gold using a sputtering device.

The distribution of the sieved sorbent beads was determined with a Coulter Counter TA II apparatus in 1 wt.-% sodium chloride solution. Further calculations were carried out using average values of the distribution curves corrected with respect to the porosity of the sorbent[5].

The interfacial tension was determined by the Harkins–Brown method[6] at the boundary between the continuous and dispersed phases before the onset of polymerization.

Mercury porosimetry was used to characterize samples with a Carlo Erba Series 2000 apparatus in the pore size range 3.74–2500 nm.

RESULTS AND DISCUSSION

Usually, the porous structure is characterized by porosity, specific surface area and pore size distribution (determined by mercury porosimetry or from the adsorption isotherm of nitrogen or other compounds). Sometimes also some anomalies in the porous structure are determined (bottle-like pores and the like). Some of these quantities may also be obtained by gel permeation techniques.

Pore size of sorbents

The exclusion limits of high-molecular-weight standards may be used in the determination of the pore size of sorbents. As can be seen in Tables II and III, values calculated from the upper exclusion limits of the individual copolymers (*r*) coincide in their order of magnitude with the average pore radii (*r̄*) calculated from the specific surface area and specific pore volume, but the absolute values are 2–6 times lower. Such an apparent discrepancy is connected with a number of factors that affect the commensurability of both methods. The *r* values predominantly reflect inlet pores of major size, while the *r̄* values represent mean values. Furthermore, the *r̄* values are considerably affected by the specific surface area values also involving micropores which cannot become operative during the penetration of macromolecular standards under conditions of gel permeation chromatography. The calculation of *r̄* requires a knowledge of the model of the porous structure, as shown below[7].

The value of *r̄* may be calculated using specific pore volumes determined from cyclohexane or water regain (Table III), the former being 21–46% lower than the

TABLE II

RELATIONSHIP BETWEEN EXCLUSION LIMIT AND PORE SIZE OF THE SORBENT

Sample	Mh_0*	n**	$r(nm)$***
1	$1.1 \cdot 10^5$	691	6.4
2	$5.0 \cdot 10^5$	3084	13.4
3	$6.6 \cdot 10^5$	4076	15.4

* Upper exclusion limit of the sorbent according to polydextran standards.

** Number of structural units of the standard.

*** Radius of the macromolecule of polydextran standard calculated from $r^2 = n\, b^2/6$, where b is the size of the structure unit (= 0.592 nm) calculated from interatomic distances.

TABLE III

COMPARISON BETWEEN POROSITY CHARACTERISTICS USING VARIOUS METHODS

Method	V_g (cm³/g)			S_g (m²/g)			p (%)*			$\bar{r}$ (nm)**		
	1	2	3	1	2	3	1	2	3	1	2	3
GPC determination	0.88	0.78	0.91	–	–	–	52	50	54	47	39	39
Water regain***	0.72	0.78	1.15	–	–	–	48	50	59	39	39	50
Cyclohexane regain***	0.39	0.62	0.85	–	–	–	33	44	52	21	31	37
Mercury porosimetry	0.81	0.55	0.86	144	65.5	125	51	42	53	141§	178§	199§
Nitrogen sorption	0.018	0.015	0.016	37.2	39.6	46.2	2.3	1.9	2.0	0.96	0.75	0.69

* Porosity calculated using eqn. 1.
** Mean pore radius calculated assuming cylindrical pore geometry.
*** Specific pore volume of the sorbent determined by regain of the medium using centrifugation techniques.
§ Mean pore radius according to the distribution curve (Fig. 4).

latter and presumably unaffected by swelling of the polymeric matrix. If the pore size determined by GPC is regarded from this standpoint, it can be seen that the differences are not that large. The largest pores (and porosity) were found with sample 3 prepared by using poly(vinyl alcohol) in a higher concentration when the interfacial tension γ was 18 mN m^{-1}, while the lowest pores were observed in sample 1 in which the concentration of poly(vinyl alcohol) during the preparation was very low, and γ was 75 mN m^{-1}. Data can be found in the literature[6] according to which the use of suspension stabilizers having a higher interfacial tension compared with other stabilizers leads to the formation of a less porous and more compact internal structure of suspension poly(vinyl chloride). The existence of direct proportionality between the interfacial tension and the size of suspension particles is also an established fact.

Porosity of the sorbent

    Using the exclusion limits of low-molecular-weight compounds which completely penetrate into the porous structure, the porosity of the sorbent may also be determined, assuming that no other interactions are operative. Correction for the interstitial column volume is necessary, however; it is known for regular spherical particles, varying between 30 and 33% of the total volume.

    Porosity is usually expressed by using the following equation and defined as the ratio between the pore volume and the total polymer volume:

$$p = \frac{V_g}{V_g + 1/d} \cdot 100 \tag{1}$$

where V_g is the specific pore volume (cm^{3}g^{-1}) and d is the polymer density ($= 1.3$ g cm^{-3}).

    If GPC is used in the porosity determination, the mass of dry polymer in the column (G) must also be known, together with the elution volumes of methanol and polydextran P2000 (V_{CH_3OH}, V_0). The porosity is then given by the equation

$$p = \frac{V_{CH_3OH} - V_0}{V_{CH_3OH} - V_0 + G/d} \cdot 100 \tag{2}$$

    Porosities determined by GPC are given in Table IV, and water and cyclohexane regains are given in Table III; the values indicate the commensurability of the two methods. The differences do not exceed 5%. Also, the porosity values obtained by mercury porosimetry are only slightly lower (1 8%), which is a good fit considering that the method can be applied to dry samples only in the pore interval 3.74–2500 nm, and that the pore volume below 3.74 nm is negligible (0.015–0.018 cm^3/g), as ensues from the sorption of nitrogen.

    The morphology of the porous structure can also be deduced from the porosity determinations. By comparing the GPC values and water regain, the accessibility of the porous structure (P) can be calculated from the equation

TABLE IV

RELATIONSHIP BETWEEN EXCLUSION LIMIT AND POROSITY OF THE SORBENT

Sample	V (cm^3)*	V_0 (cm^3)**	V_i (cm^3)	G (g)***	p $(\%)$§	P $(\%)$§§
1	53.2	30.9	22.3	25.4	52	110
2	55.1	37.3	17.8	22.7	50	100
3	57.9	40.1	17.8	19.4	54	91

  * Exclusion limit of methanol.
 ** Exclusion volume of polydextran D 2000.
*** Weight of dry sorbent in the column.
  § Porosity from GPC data calculated using eqn. 2.
 §§ Accessibility of porous structure calculated using eqn. 3.

$$P = \frac{\dfrac{dV_\ell + 1}{dV_\ell}}{\dfrac{d(V - V_0) + G}{d(V - V_0)}} \cdot 100 \tag{3}$$

Measurements suggest (Table III) that with sample 3, prepared with 2% (w/w) of poly(vinyl alcohol) in the continuous phase, one part of the porous structure is inaccessible to the gel permeation process, in spite of the fact that the interfacial tension between the continuous and dispersed phases at the beginning of the polymerization is in fact at its lowest, and thus the structure of the matrix should be in its loosest state.

Geometry of the porous structure

Another problem with characterization of the porous structure is its geometry. The factor involving the pore geometry is included in the relationship used in the calculation of the distribution coefficient:

$$K_{calc} \cdot \left(1 - \sigma \cdot \frac{r}{\bar{r}}\right)^2 \tag{4}$$

where $\sigma = 1,2$ or 3 for tubular, cylindrical or spherical pores, respectively, r is the size of the molecule of the standard and $\bar{r}$ is the pore size as mentioned above.

Values of the distribution coefficients thus calculated were compared with those obtained experimentally from the elution volumes, V_e, using the equation

$$K_{exp} = (V_e - V_0)/V_1 \tag{5}$$

in which V_0 is the void volume and V_i is the internal volume of the pores. Dependences of the distribution coefficients shown in Fig. 1 correspond to the pore geometry valid for cylindrical and spherical pores ($\sigma = 2$ and 3, respectively).

The geometry of the porous structure may be perturbed by various irregularities and disturbances which then become operative according to their extents. Closed pores decrease the experimentally determined values of the distribution coefficient
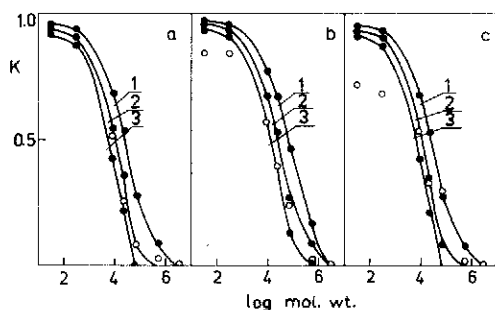
Fig. 1. Relationship between the distribution coefficient and pore geometry. Curves: 1, $\sigma = 2$; 2, $\sigma = 3$; 3, $\sigma = 4$ [in the equation $K = (1 - \sigma r/\bar{r})^2$]. O, Experimental values.

compared with the calculated values; bottle-like pores, one-side-open pores and shells cause the same values to increase.

Under conditions of GPC, the character of the porous structure is also reflected in the broadening of the peak. The chromatographic peak may also become wider owing to the adsorption and convection of molecules in the pores. As the $V_e - V_0$ values of the standards used do not exceed the pore volume of the sorbent in the column, any role played by adsorption with these sorbents and solutes may be ruled out.

Information on the possible role played by the individual terms of the equation describing the height equivalent to a theoretical plate (HETP, H) is provided by an analysis of this equation in a simplified form[8]:

$$H = A + B/u + Cu \qquad (6)$$

where A involves the contribution of turbulent diffusion, B involves that of molecular diffusion and C reflects the effect of the flow-rate on the velocity profile effects. Even though the above equation does not describe the respective factors in a complex way,

TABLE V

RELATIONSHIP BETWEEN WIDENING OF THE CHROMATOGRAPHIC PEAK AND MORPHOLOGY OF THE POROUS STRUCTURE

Sample	Constants of eqn. 6*			H_{perm}^{flow} (cm)**		γ***		Peak asymmetry§	
	A	B	C	Calculated	Determined	Methanol	D 70	Methanol	D 70
1	−0.221	416.4	0.011	$1.96 \cdot 10^5$	2.0	0.0054	—	0.875	0.627
2	1.034	49.87	0.0057	48.68	0.5	0.0054	0.037	0.625	0.630
3	0.831	0.041	0.0072	30.67	2.4	0.0014	0.026	0.520	0.554

* Constants representing the contribution of turbulent molecular diffusion and "velocity profile effects" to the HETP calculated using eqn. 6 by employing a procedure in ref. 8.
** HETP of permeation dispersion calculated using eqn. 7; HETP calculated using $H_{exp} = (4V_e/\omega)^2/l$, where ω is the peak width at zero line and l is column length.
*** Obstruction factor γ, calculated using the equation given in the Appendix.
§ Peak asymmetry was determined from the ratio of intercepts cut out at one tenth of the peak height by a perpendicular drawn from the top of the peak to the zero line.
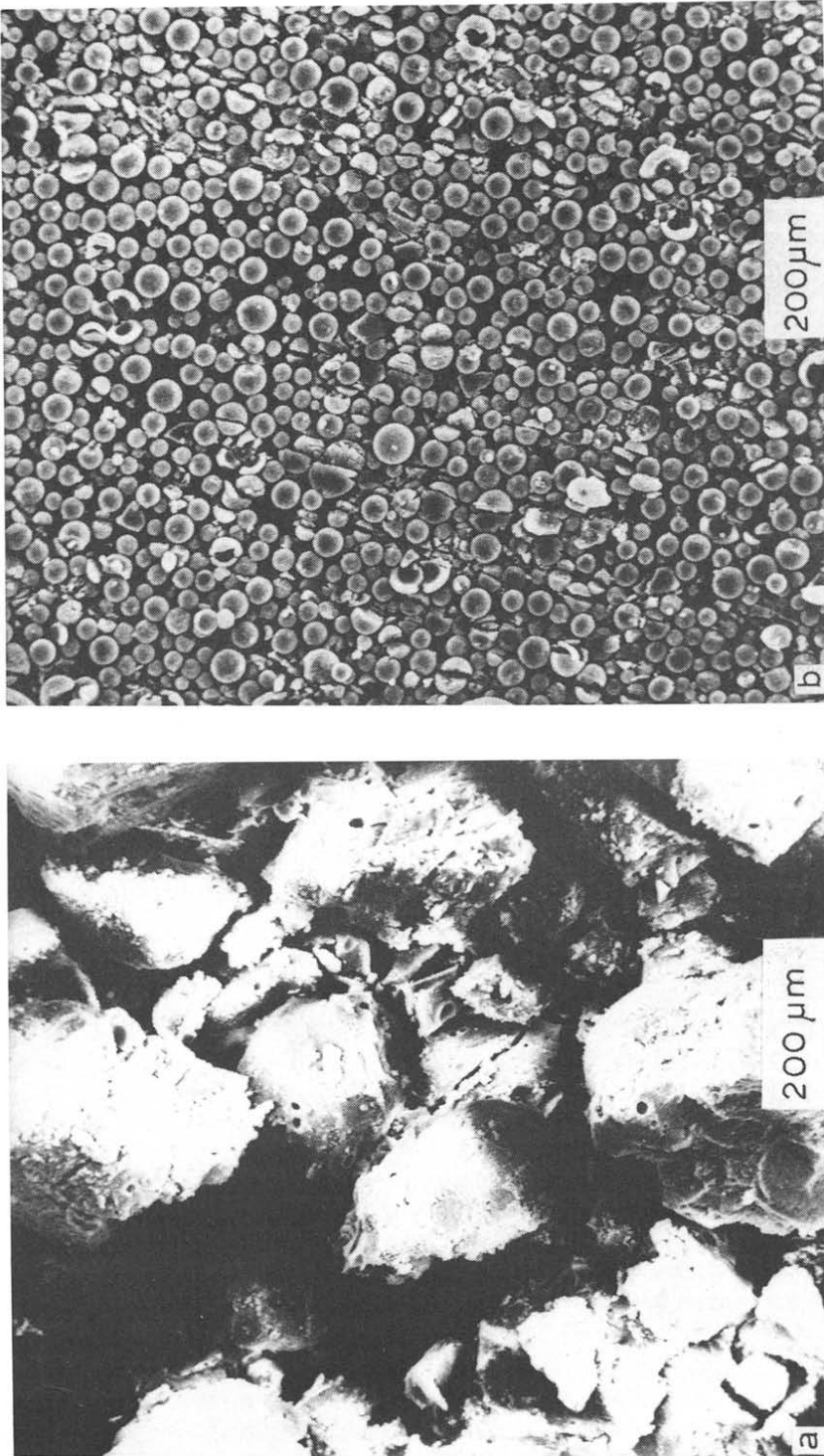
Fig. 2. Appearance and surface morphology of beads of samples 1 (a) and 3 (b) of macroporous glycidyl methacrylate ethylene dimethacrylate copolymers.

it can be seen from Table V that with samples 1 and 2 the largest contribution is that of molecular diffusion, whereas with sorbent 3 it is provided by turbulent diffusion. The remaining terms can be neglected compared with the predominant effect; this is especially true for the effect of the flow-rate on the velocity profile effects.

In convection transport[9] (see Appendix), which plays the main role in sorbents the pores of which are larger than the interstitial ones, the HETP of permeation dispersion (H_{perm}^{flow}) is given by

$$H_{perm}^{flow} = \frac{4V_0 K \; V_j \mu d_p}{V_e^2 u_s'} \tag{7}$$

where u is the linear flow-rate in the column, u_s' is the linear flow-rate in the pores and d_p is the diameter of the sorbent particles.

As the flow-rate inside the pores cannot be determined directly, u/u_s' must be replaced by $d_p/2.3 \; r$. The values of the pore and particle sizes show that the basic condition for dynamic fractionation remains unsatisfied, which is only confirmed by the H_{perm}^{flow} values summarized in Table IV. The calculated values exceed the experimental values by several orders of magnitude. Hence, the convection transport in the pores can be neglected compared with the diffusion transport under given conditions, and it is therefore possible, using the relationship for variation of the peaks, to determine the diffusion coefficient of the solute in the sorbent and by comparing it with the diffusion coefficient of the solute in solution to determine the obstruction factor (Table V, Appendix).

Values of the obstruction factor determined by using methanol and dextran D 70 are comparatively low, which suggests that diffusion is considerably impeded by the porous structure; it should be borne in mind, of course, that the accuracy of determination is affected by the high polydispersity of the dextran used (M_w/M_n = 1.7) and by the high diffusion coefficient of methanol. Of the samples taken for investigation, the diffusion is most strongly impeded in sample 3 prepared in a 2% aqueous solution of poly(vinyl alcohol), at the interphase tension of 18 mN m^{-1}. The obstruction coefficients of samples 1 and 2, where the interphase tension at the beginning of polymerization was higher, viz., 75 and 41 mN m^{-1}, respectively, are also higher.

Theoretically, the obstruction coefficient could also be used in the determination of the tortuosity of the pores, but again the problem of the model of porous structure occurs.

The appearance and surface morphology of samples 1 and 3 are characterized by Figs. 2 and 3. Whereas with 0.007% (w/w) of poly(vinyl alcohol) we failed to obtain regular beads (sample 1, Fig. 2a), at higher poly(vinylpyrrolidone) and poly(vinyl alcohol) concentrations regular beads were prepared (sample 3, Fig. 3a). The compactness of the surface shell was examined in greater detail at high magnification (10,000). The difference between values of the obstruction factors of these samples can be readily explained through the larger surface compactness of sample 3 compared with sample 1 (Fig. 3a and b).

The asymmetry of peaks obeys the same dependence as the obstruction factor. Obviously, the asymmetry of peaks has only a semiquantitative character, because
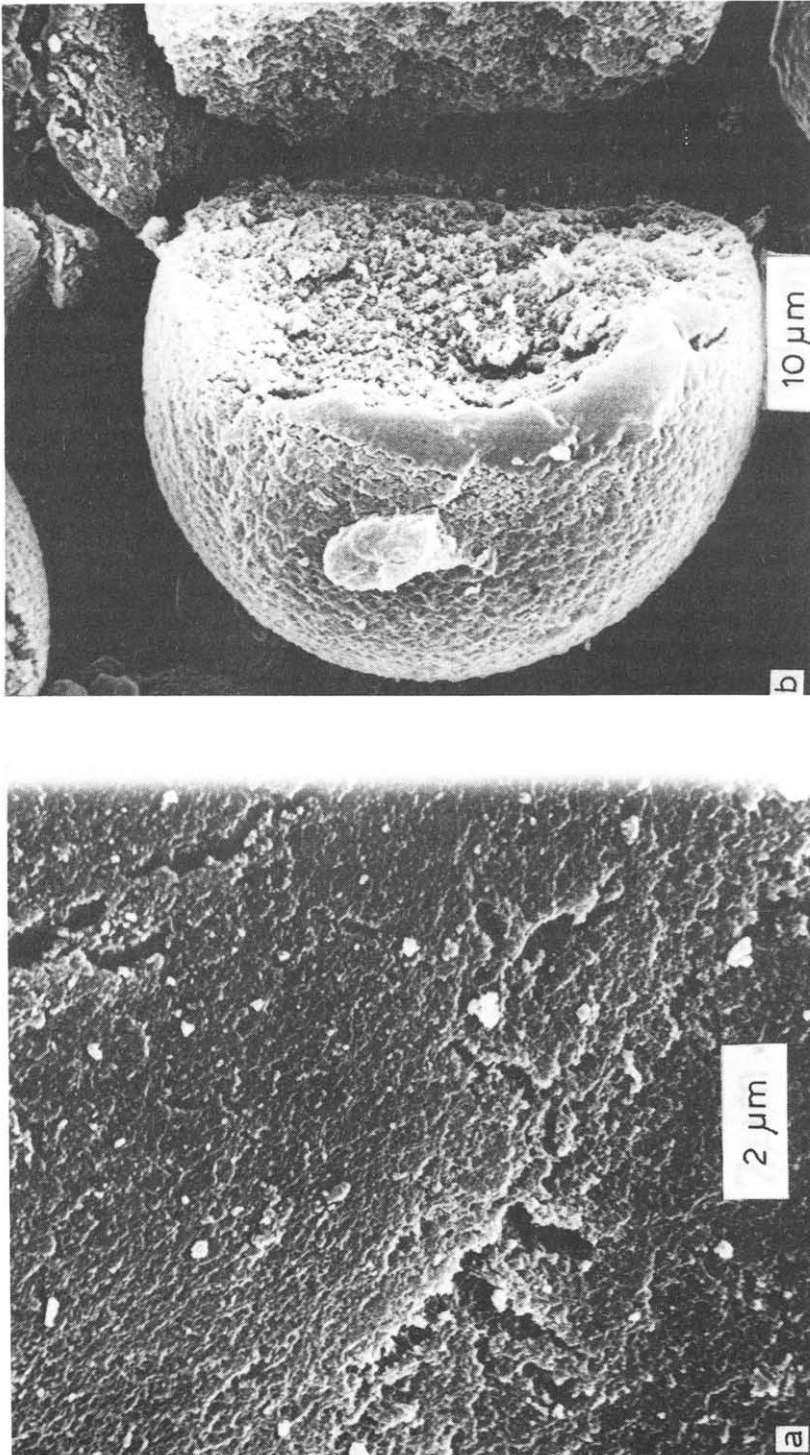
Fig. 3. Comparison between surface compactness values of samples 1 (a) and 3 (b) of macroporous glycidyl methacrylate ethylene dimethacrylate copolymers.

its physical interpretation is indirect and restricted; its advantage is that it is easy to determine. With the sorbents under study the highest peak symmetry in the determination with methanol was observed with sorbent 1 prepared from 0.007% (w/w) of aqueous poly(vinyl alcohol), and the lowest was found with sample 3, when the poly(vinyl alcohol), and the lowest was found with sample 3, when the poly(vinyl alcohol) concentration in water was 2 wt.-%. As the peak symmetry of polydextran D 2000 is virtually the same with all sorbents, while polydextran does not penetrate into the porous structure, and the peak asymmetry observed with methanol reflects properties of the porous structure.

Relationship between the distribution coefficients and pore distribution

The possibility of the determination of the pore distribution of porous materials ensues from the theory of the equilibrium distribution of rigid molecules of the solute under conditions of the exclusion of molecules worked out by Giddings *et al.*[10]. As early as in 1975, however, Halasz and Kornel[11] suggested the use of exclusion chromatography for the determination of pore distribution; using rigid sorbents (silica gel), they refined the method and compared it with the results of classical methods[12]. Halasz and Martin[13] also defined its boundary conditions and pointed out the possibility of its utilization with swelling sorbents based on polymers[14]. For the practical solution of the problem of pore distribution in macroporous styrene–divinyl benzene copolymers, this method was applied by Freeman and Poinescu[1] who also introduced the term "inversion gel permeation chromatography". Kuga[14] applied these methods to dextran gels.

The method is based on the determination of the dependence between the size of molecules of the solute, exclusion volume and distribution coefficients. The problem is that one has to know the geometry of the porous structure of the sorbent and the relationship between the distribution coefficients and the size of molecules of the solute[14]. The calibration dependence of molecular weight on the radius of the molecules is well satisfied both for the radius calculated from structural units and for the hydrodynamic parameters (the difference being 0.1 nm at most). Transformation of the distribution coefficients to the fraction of pore volumes accessible to the particular solutes followed by a plot against the size of their molecules gives the overall pore size distribution curves (Fig. 4). With macroporous copolymers of glycidyl methacrylate and ethylene dimethacrylate, these dependences are identical for polydextrans
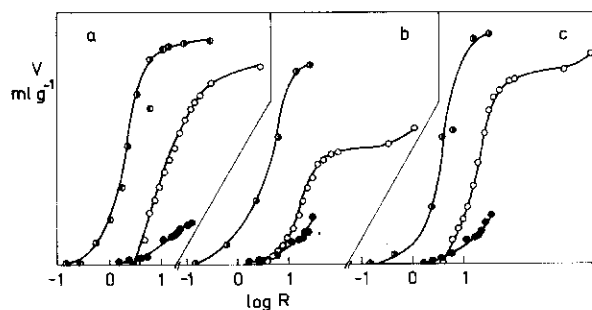

Fig. 4. Pore distribution of samples 1 (a), 2 (b) and 3 (c) determined by GPC. [◑ Polydextrans; ◐ poly(ethylene glycols)], mercury porosimetry (○) and sorption isotherm of nitrogen (●).

and polyethylene glycols. The mean distribution value determined by GPC agrees well with the mean pore radius calculated from the pore volume obtained from the cyclohexane regain and specific surface areas (2–5 nm, Table III). As regards the course of the distribution itself in these samples, it can be said that sample 1 differs from the other two mainly by the effective pore size (90% of pores are smaller than 5.4 nm; in the other two, the respective values are below 10 nm). The distribution has the same shape for all samples under investigation.

The mean pore size values determined by mercury porosimetry differ considerably from the preceding ones (by 10–15 nm). No agreement with the distribution curve from GPC resulted from supplementing mercury porosimetry by the sorption isotherm of nitrogen. These differences are obviously due to the different physical state of copolymers and may be explained through the closing of small pores on drying. Although there are certain reservations concerning the pore distribution from GPC data[15,16], it should be borne in mind that this is the only possible method of determination with swelling polymers[14,17]. The study has demonstrated that in strongly cross-linked copolymers with limited swellability changes occur in both the pore volume and distribution in the swollen and dried states.

APPENDIX

According to the theory of GPC, the following influences may become operative under the conditions used[10]:

(a) adsorption and non-ideal behaviour of molecules of the solute;
(b) diffusion of molecules in internal pores;
(c) convection of molecules in internal pores; and
(d) the behaviour of molecules in interstitial spaces.

These processes increase the elution volume and/or cause widening of the chromatographic zone of the peak, which may be described by a general equation. With a free choice of the solute and under conditions of GPC the effect of the solute is small, and for the variation[10,18,19] of peak widening due to the permeation process (μ_2) we obtain

$$\mu_2 = \frac{1}{30} \cdot \frac{K_{exp} V_i \, V \, d_p^2}{D_s}$$

where K_{exp} is the distribution coefficient, given by

$$K_{exp} = (V_e - V_0)/V_i$$

where V_e is the elution volume of the standard (cm³), V_0 is the free volume between particles of the packing (cm³), V_i is the internal pore volume of the sorbent (cm³), V is the flow-rate of water (cm³ sec⁻¹) and d_p is the diameter of sorbent beads (cm).

This expression can be used in the determination of the diffusion coefficient of the solute in the sorbent, D_s, related to the diffusion coefficient in solution, D, by the obstruction factor γ:

$$\gamma = D_s/D$$

This coefficient reflects the hindrance to penetration into the porous structure of the sorbent and is related to the coefficient of pore tortuosity proportional to the porosity of the sorbent; the proportionality is given by the shape of the pores.

Hence, under certain conditions, the obstruction factor may adequately reflect irregularities in the porous structure, such as impenetrable pores and surface shell.

SYMBOLS

r pore radius according to the exclusion limits of polydextrans, $r^2 = nb^2/6$ (nm);

$\bar{r}$ mean pore radius, $r = 2000\, V_g/S_g$;

R pore radius

b dimension of structural unit (polydextrans, $b = 0.592$ nm);

n number of structural units;

V_g specific pore volume from cyclohexane or water regain (cm^3/g);

S_g specific surface area of the sorbent (m^2/g);

p porosity of the sorbent (%);

V_{CH_3OH} exclusion volume of methanol under GPC conditions (cm^3);

V_0 upper exclusion volume (usually for polydextran D 2000) (cm^3);

G weighed amount of dry copolymer in the column (g);

d polymer density (g/cm^3);

P accessibility of porous structure (%);

K_{calc} distribution coefficient, $K_{calc} = (1 - \sigma \frac{r}{r})^2$, where σ is a factor including pore geometry;

K_{exp} distribution coefficient according to GPC data, $K_{exp} = (V_e - V_0)/V_i$;

V_e elution volume of measured solute;

V_i internal pore volume of the sorbent;

H height equivalent to a theoretical plate (HETP) (cm);

A contribution of turbulent diffusion;

B contribution of molecular diffusion;

C effect of flow-rate on the profile of penetration curve;

u linear flow-rate in the column (cm/sec);

u'_s linear flow-rate in pores (cm/sec);

d_p diameter of sorbent beads;

V flow-rate (cm^3/sec);

D_s diffusion coefficient of solute in the sorbent;

D diffusion coefficient of solute in solution;

γ obstruction factor;

H_{perm}^{flow} HETP of permeation dispersion;

μ_2 variation of peak widening due to permeation process;

ω peak width at zero line;

l column length.

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