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APPLICATION OF POROUS GLASSES FOR GEL CHROMATOGRAPHY OF POLYMERS

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SUMMARY

The basic principles of obtaining and controlling porous structure of glasses with large pores were formulated and the possibility of using these glasses for gel chromatography of polymers was demonstrated.

It was established that the curve of polystyrene elution does not correspond to the curve of the pore distribution in glass. Moreover, a part of porometrically accessible pores does not participate in the separation of the macromolecules, the pores whose size corresponds to the radius of gyration of macromolecules in this solvent being inaccessible to these macromolecules.

Porous glasses are very promising materials for gel chromatography of polymers[1]. This paper deals with the basic principles of formation and control of the porous structure of glasses with large pores. Relationships between their structural parameters and the size and elution characteristics of macromolecules have also been investigated.

The products known as "porous glasses" are usually obtained by treating sodium borosilicate glasses capable of opalescence with acid solutions. The development of opalescence in these glasess when they are kept within a certain temperature range is due to their separation into two microphases of different composition. One of them is rich in silica and the other one mainly consists of borate. The exact composition of each phase is regulated by the composition of the glass and the temperature at which it is maintained in the opalescence zone. Since borates and B_2O_3 are soluble in acids, these components of the borate phase (under conditions of its steric continuity) are removed selectively from the glass by treatment with acids leaving a system of canals and pores in the leached glass. That is the reason why the pore size and volume depend on the amount of B_2O_3 and Na_2O passing from the glass into solution during the acid treatment. These amounts, in their turn, depend on the composition of the respective phases of the glass and on the peculiarities of its phase distribution.

Usually, the pore diameters in porous glasses obtained by a simple acid treatment vary approximately from 15 to 100 Å and the pore volumes vary from 0.10 to 0.25

cm^3/g. The structural characteristics of a porous glass can be controlled by varying the composition of the glass and the conditions of heat treatment within these limits. Sodium borosilicate glasses capable of forming a porous glass contain only a limited amount of acid-soluble material (B_2O_3 and Na_2O). Owing to this fact, attempts to obtain porous glasses with large pores by acid treatment have failed. The possibility of preparing such porous glasses has been reported earlier[2], it consisted of a supplementary treatment of the porous glass with solutions of 0.5 *N* KOH or NaDH at room temperature.

It was shown[2] that this treatment resulted in a considerable increase in both the pore volume and the pore size. The changes observed in the structure of porous glasses are quite different for initially transparent and opalescent sodium borosilicate glasses. In both cases alkali treatment produced an approximately equal (a 4–5-fold) increase in the pore volume but for opalescent glass the increase in the pore size was much greater than for the transparent one. Typical differences in the structure of porous glasses after alkali treatment of transparent and opalescent glass are illustrated by adsorption isotherms and curves of the pore volume distribution (by radii) (see Fig. 1).

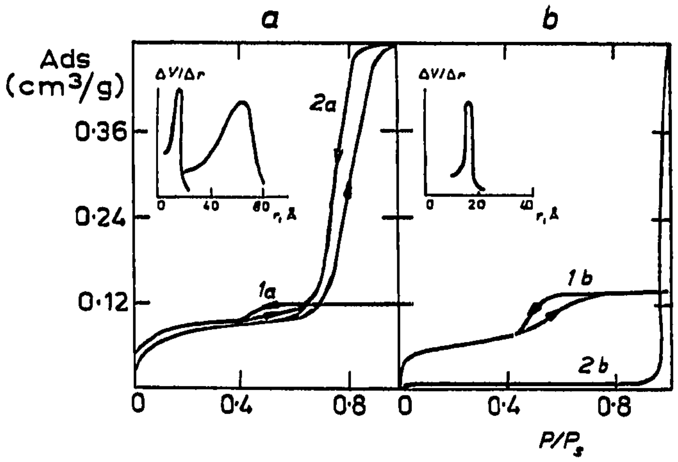

Fig. 1. Adsorption isotherms of C_2H_5OH on porous glasses obtained from transparent (a) and opalescent (b) glasses before (1a and 1b) and after (2a and 2b) their alkali treatment. In the insets, curves of the pore radii distribution are shown.

Particular changes in the structure of porous glasses after alkali treatment were accounted for[2] by assuming that the skeleton of the porous glass had a bidisperse structure. It is formed by a silica framework (skeleton) with large pores and relatively thick walls. Within these pores is situated a considerable amount of silica with a fine network structure forming the actual thin pore structure. In porous glasses obtained by the treatment of the original sodium borosilicate glasses with acids the adsorption measurements only reveal the fine pore structure while the structure of the large pore framework remains masked. However, by careful treatment with alkali one can dissolve the fine silica network of porous glass and destroy the fine structure formed within the framework without affecting the framework itself. The structure of the silica framework is directly revealed in the glass with the large pores obtained in this manner.

The conception of the bidisperse structure of porous glasses suggested earlier[2] was later confirmed by the small-angle X-ray scattering[3,4] and electron microscopy[5].

The nature of the finely dispersed silica in porous glasses and the bidisperse structure of their framework find a comprehensive explanation in terms of metastable liquation or of the immiscibility in sodium borosilicate glasses[6-10]. In accordance with the theory of metastable liquation, the borate phase of the inhomogeneous sodium borosilicate glasses should always contain not only B_2O_3 and Na_2O but also some SiO_2. Its quantity in this phase depends on the composition of glass and the conditions of its heat treatment. This silica forms the fine pore structure within the main silica framework. The amount of this silica in the borate phase determines a possible increase in the pore volume in the porous glass after alkali treatment. The pore size after this treatment will depend on the size of the "particles" of the borate phase or on the state of phase separation in the glass. The composition of the phases in the inhomogeneous glass and the size of the borate bodies are determined by the temperature and duration of the heat treatment of the glass in the region of metastable liquation. Consequently variation of the conditions of the heat treatment is a very efficient method for regulating not only the structure of glasses with small pores, obtained by acid treatment, but also the structure of glasses with large pores obtained by the alkali treatment of the porous glasses.

The porograms in Fig. 2 and the curves of the pore volume distribution *vs.* logarithms of their radii in Fig. 3 demonstrate the possibility of controlling the porous structure of glasses with large pores just by varying the conditions of the heat treatment of the sodium borosilicate glass. This method enables us to obtain, with good reproducibility, porous glasses with large, small and intermediate pore sizes and volumes.

The wide possibilities of being able to control the structure of porous glasses, their stability in various solvents and the absence of swelling make the use of such

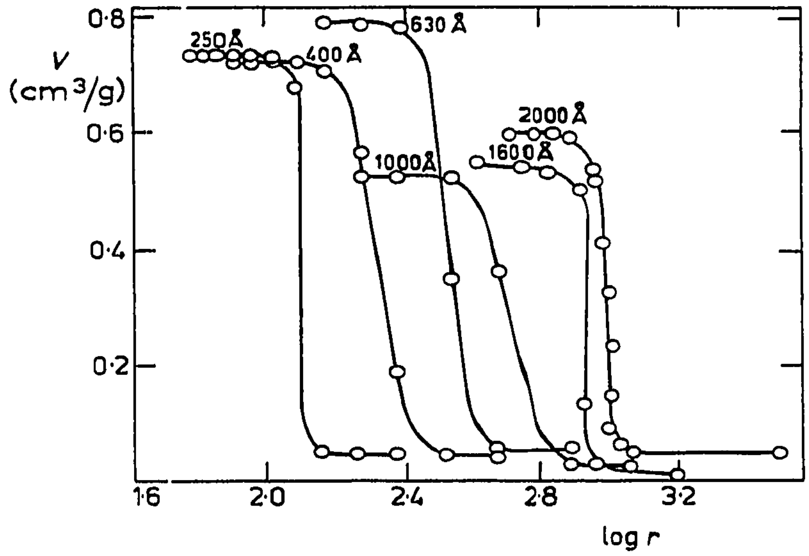

Fig. 2. Porograms of samples of glasses with large pores.

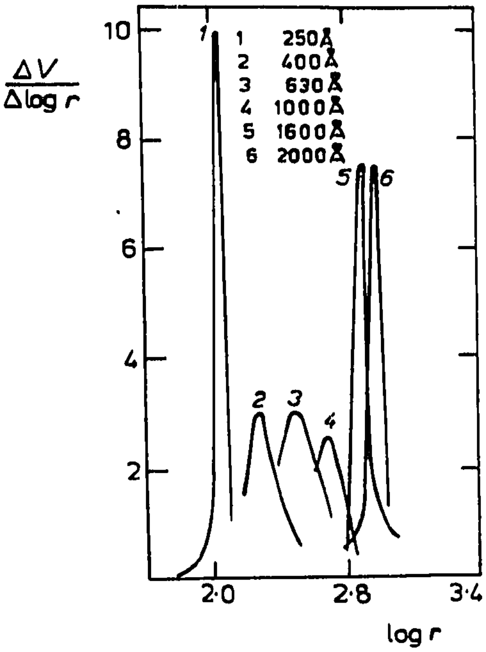

Fig. 3. Differential curves of pore distribution *vs.* the logarithm of their radii (according to Fig. 2). Å values in Figs. 2 and 3 are the pore diameters.

TABLE I

CHARACTERISTICS OF POLYSTYRENES USED

The perturbed dimensions of PS molecules in toluene were calculated from PTITSYN-EIZNER's equation[13] using experimental data for PS in toluene found in ref. 16.

Polystyrenes	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	$M_{peak} \times 10^{-4}$	M_w/M_n	$(\overline{h_0^2})^{1/2}$ Å (*cf. ref.* 12)	$(\overline{h^2})^{1/2}$ Å (*cf. ref.* 13)	$(\overline{R^2})^{1/2}$ Å (*cf. ref.* 14)	$(\overline{H})$ Å (*cf. ref.* 15)	$(\overline{Q})$ Å (*cf. ref.* 15)
Styrene	–	0.0106	–	–	–	–	–	5.5	–
ST-25169	0.50	0.46	0.48	1.09	48.2	56.2	22.9	78.5	39.4
ST-25171	1.03	0.97	1.00	1.07	69.7	85.3	34.8	119.5	59.7
ST-25168	1.985	1.965	1.975	1.02	97.8	126	51.4	176	88.2
ST-25170	5.10	4.90	5.00	1.05	156	214	87.4	300	150
ST-41995	9.82	9.62	9.72	1.03	215	324	132	453	227
ST-41984	17.3	16.4	17.1	1.06	288	437	178	611	306
ST-25166	41.1	39.2	40.2	1.05	442	725	296	1015	508
ST-25167	86.7	77.3	83.0	1.13	635	1100	449	1540	770
ST-61970	214.5	178.0	198.7	1.2	978	1780	726	2490	1250
PS-No. 1 fr. 2	1100	–	–	–	2310	4900	2000	6850	3430
PS-No. 1 fr. 1	1600	–	–	–	2860	6020	2460	8410	4220

porous glasses very promising in liquid chromatography for separating mixtures of substances with molecules of different size. We have used macroporous glasses successfully for fractionating polymer mixtures with respect to their molecular weight.

Experiments have been carried out with a liquid chromatograph ChL-1302 (U.S.S.R.) with a refractometer detector. Porous glasses were placed in chromatographic glass columns 120 cm in length and 8 mm in internal diameter. The columns were filled by the method recommended in ref.11. Experiments were carried out in toluene at 20° and the elution rate was 50 ml/h. The sample volume was 1 ml of a polymer solution at a concentration of 0.5 g/100 ml. Standard samples of polystyrenes (Waters Associates) and two samples of high molecular weight polystyrene were used. Their characteristics are given in Table I.

The porous glasses described proved to be quite suitable for the gel chromatography of polymers. This can be seen from Fig. 4 which shows the results of chromatographing a polystyrene mixture using four columns with porous glasses Zh-130, Zh-250, Zh-700 and Zh-1600, their mean pore diameter is 130, 250, 700 and 1600 Å, respectively. We obtained a relationship between the reduced volumes and the size of the macromolecules, for each porous glass.

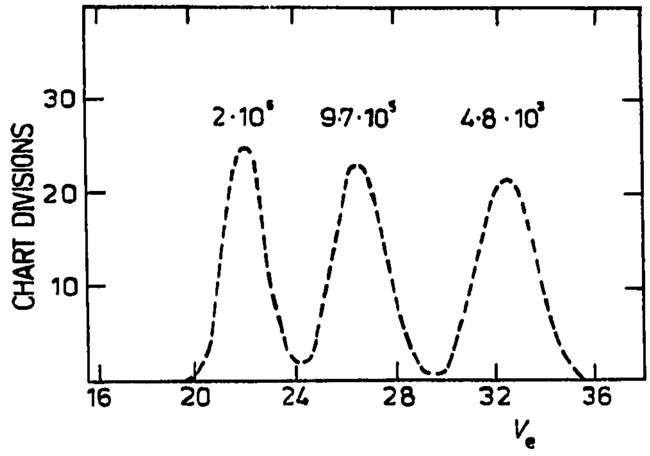

Fig. 4. Gel chromatogram of standard polystyrenes with molecular weights 4.8 × 10^3; 9.7 × 10^5 and 2.0 × 10^6 on four columns with porous glasses Zh-130, Zh-250, Zh-700, Zh-1600. Solvent: toluene; elution rate: 50 ml/h, temperature: +20°; sample volume: 1 ml at a concentration of 0.2 %.

This relationship is shown in Fig. 5 together with the respective porometric curves*. The calibration curves in this figure were obtained by subtracting from the reduced volume (V_e) the free volume (V_0) of the column which was assumed to be equal to the reduced volume of polystyrene with a MW = 1.6 × 10^7. The porometric curves are given without the lower flat part which refers to the spaces between the sorbent particles, *i.e.* to V_0. Thus, Fig. 5 permits the evaluation of the ratios of the reduced volume to the porometric pore size distribution.

One of the main problems in GPC is the ratio of the size of macromolecules to the gel pores. It is generally assumed[17] that those pores whose size exceeds the mean square end-to-end distance of the chain by not less than twofold are accessible.

This relationship was not confirmed in our experiments. In columns with the

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* Similar results have been obtained with silica gels[22].

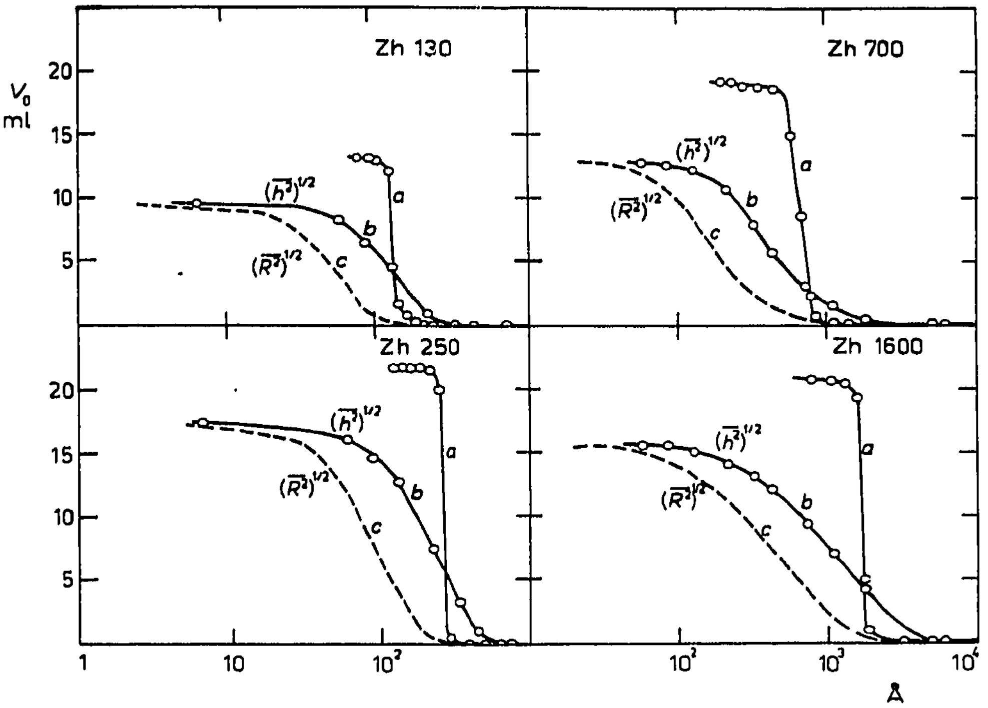

Fig. 5. Porometric curves (a) for glasses with large pores Zh-130, Zh-250, Zh-700, Zh-1600 in the amounts of 54.9, 30.9, 42.2, and 38.2 g in columns 1.2 m in lenght and 0.8 cm in diameter and of the corresponding elution curves of PS with different MW, characterised by mean square end-to-end distance (b) and mean square radius of gyration (c). Solvent: toluene; elution rate: 50 ml/h; temperature: 20°.

glasses: Zh-130, Zh-250, Zh-700 and Zh-1600, the pore whose size is commensurable with the radius of gyration of a macromolecule* does not participate; this finding may be interpreted in two ways. Either the macromolecules in pores are greatly deformed (they have changed their size by several times) or on approaching the pores they are oriented in such a way that their least mean size P is placed in front of the narrowest part of the corresponding pore.

A comparison of our results with porometric data shows that not all the accessible pores take part in the chromatographic process.

Moreover, the number of accessible pores which do not take part in the process increases with the size of the macromolecules. It is reasonable to assume that these pores are the deep ones, *i.e.*, that they are located relatively far from the surface of the sorbent particles.

The porous glasses with a narrow pore size distribution which were used in our work permitted us to establish the fact that the molecular sieve effect does not play a major part in the chromatographic separation of macromolecules since it is possible to separate macromolecules for which the porous glasses have the same size of accessi-

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* Polystyrene molecules in solution are known to be bean-shaped and are characterised in three mutually perpendicular dimensions by sizes $(\bar{h}^2)^{1/2}$; $(\bar{g}^2)^{1/2}$; $(\bar{p}^2)^{1/2}$ (ref. 18) which are interconnected by the ratio $(\bar{h}^2)^{1/2}:(\bar{g}^2)^{1/2}:(\bar{p}^2)^{1/2} = 2\sqrt{6}:2:1$. Moreover, the mean maximum size of the coil is determined by $\bar{H} = 1.4(\bar{h}^2)^{1/2}$, the mean maximum transverse size — by $\bar{Q} = 0.7\,(\bar{h}^2)^{1/2}$ (ref. 15). The radius of gyration of macromolecules is $(\bar{R}^2)^{1/2} = 1/\sqrt{6}\,(\bar{h}^2)^{1/2}$ (ref. 14), this is close to the mean maximum transverse size in the third direction $\bar{P}$.

ble pores. This separation can proceed only owing to the diffusion factor which was taken into account in refs. 19 and 20 as well as in another paper[21] read at this seminar. In this paper[21], the diffusion effect was determined by two factors exp $[-u^2r^2/\zeta D^2]$ and $[1 - (u^2\tau^2/\sigma^2)]$ where u is the elution rate, D is the coefficient of translational diffusion of the macromolecules, r is the mean radius of the canals between the sorbent particles, σ is the dispersion of the chromatographic peak, τ is the value characterising the non-equilibrium of the process. The first of these factors is responsible for diffusion effects in the mobile phase, the second one also includes diffusion effects in the stationary phase, since the value τ is a function of the diffusion coefficient D' of macromolecules in the sorbent phase:

$$\tau = B \times a^2/D'$$

where a is the depth of penetration of the macromolecules into the sorbent grains, and B is a certain geometrical constant.

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