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INFLUENCE OF THE STRUCTURE OF MACROPOROUS GLASSES ON THE SEPARATION OF POLYMERS BY GEL PERMEATION CHROMATOGRAPHY

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SUMMARY

The gel permeation chromatographic separation of polystyrenes has been studied on columns of macroporous glass beads differing in the particle size and the pore volume. Macroporous glass beads have been prepared according to the method given in ref. 7 which is described in detail in ref. 2.

The possibility of suppressing polymer adsorption on the surface of macroporous glass beads is shown by the addition of small quantities (1–2 %) of the adsorption-active substances (*e.g.* tetrahydrofuran) to the eluent. A significant increase in the effectiveness of gel permeation chromatography with increasing pore volume of macroporous glass is observed. The combination of chromatographic columns packed with macroporous glass beads of different sizes which provides the linear calibration relationship in the molecular weight (M) range of $5 \cdot 10^3$–$2 \cdot 10^6$ is found. The chromatographic columns of macroporous beads are shown to be no less effective in separating narrow fractions of polystyrene than the styrogel columns of Waters Associates.

INTRODUCTION

Gel permeation chromatography (GPC) is the most important method used for the analytical control of polymers at present. It enables information about the molecular weight characteristics of polymers to be obtained in a relatively short time by using comparatively small amounts of sample. The method is based on the fractionation of macromolecules according to their sizes on porous sorbents. Organic sorbents (styrogels, copolymers of styrene and divinylbenzene) are generally used as the porous sorbents. Recently, inorganic sorbents have been used in GPC, such as macroporous silica gels and porous glasses. In contrast to hydrophobic organic gels (styrogels, etc.), these inorganic sorbents possess high mechanical strength, show low resistance to the eluent flow, have high thermal stability, and do not swell in organic solvents. An extremely useful property of inorganic sorbents is the possibility of measuring, by an independent method, for example with the aid of mercury intrusion, the volume of pores and their size distribution, thus giving possibilities for a detailed study of the GPC mechanism[1].

At the same time, many of the questions concerning the use of inorganic sorbents for GPC remain unclear. In particular, the influence of the porous structure on the chromatographic efficiency of these sorbents has been insufficiently studied. The presence of active functional groups on the surface of sorbents can lead to the appearance of adsorption interaction between these groups and the eluted macromolecules, and, as a result, to the dispersion of chromatographic peaks and to the breaking of the ideal regime of GPC. In this connection, the elucidation of the possibilities of suppressing the surface adsorption activity of inorganic sorbents is of great importance.

In recent years, of the inorganic sorbents used for separating macromolecules, macroporous glasses have become widely used[2,3].

The present work had two purposes: to study the efficiency of chromatographic columns for GPC with macroporous glasses differing in their porous structures, and to investigate the possibilities of suppressing the adsorption of polymers on the surface of porous glass by adding adsorptive components to the eluent.

STRUCTURE AND METHODS OF PREPARATION OF MACROPOROUS GLASSES

Porous glasses, which were developed independently and simultaneously in the U.S.S.R. by Grebenshchikov and in the U.S.A. by Hood and Nordberg, are porous products obtained by the treatment of two-phase sodium borosilicate glasses with acid. By varying the composition of the initial glass and the conditions of its thermal and chemical treatments[4], porous glasses of very different structures can be obtained. However, the pore sizes of porous glasses obtained by the treatment of sodium borosilicate glasses with acid usually cover only a comparatively narrow range, from 10 to 150 Å, and the pore volumes vary from 0.10 to 0.25 cm^3/g. Various examples of the applications of such microporous glasses in gas chromatography have been described[5,6].

Essentially new possibilities for applications in chromatography were found for macroporous glasses obtained from microporous ones by treatment with moderately concentrated alkaline solutions according to the method suggested by ZHDANOV[7].

The structure of macroporous glass appears to be closely connected with phase separation in the initial sodium borosilicate glass, and can be extremely effectively and finely regulated by changing the composition of the initial glass and the conditions used in its treatment. This provides a method of obtaining macroporous glasses with pore sizes from 150 Å to several thousand Ångströms and with pore volumes from 0.5 to 1.5 cm^3/g and greater.

The electron micrographs in Fig. 1 show (a) the structure of the silica skeleton of the macroporous glass and (b) the change that results from heat treatment of the initial glass at 700 for 24 h. It can be seen that the pore size increased significantly as a result of such treatment, together with a thickening of the skeleton walls.

Macroporous glasses possess a non-swelling rigid skeleton with high mechanical strength, thermal stability and chemical resistance in acidic media.

With wide possible variations in the pore sizes and pore volumes, macroporous glasses show narrow curves of the pore volume distribution *versus* the pore radii (Fig. 2), which is an advantage in comparison with other silica sorbents. These features of macroporous glasses make them convenient materials for use in investigating the dependence of the chromatographic efficiency of the sorbent on its porous structure.

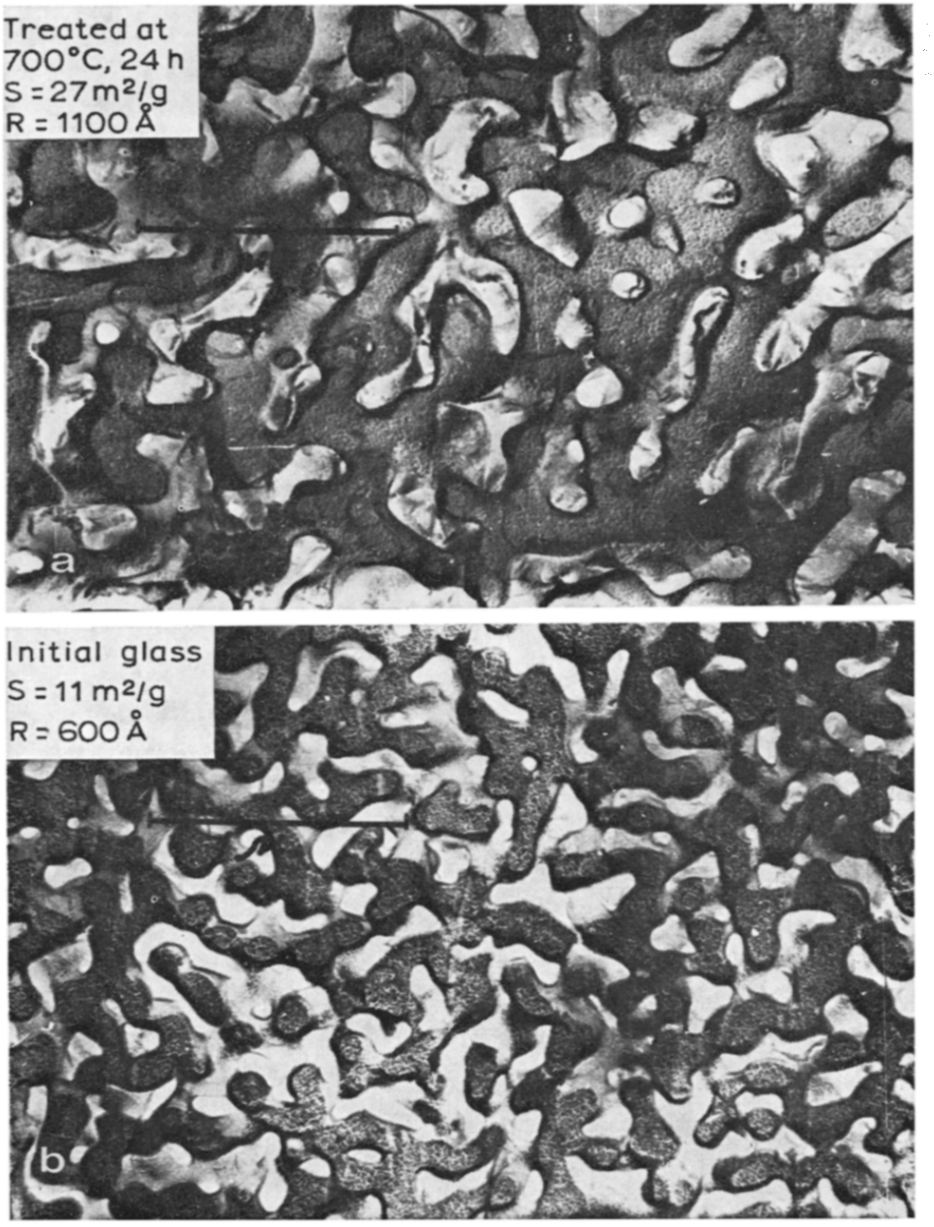

Fig. 1. Electron micrographs of macroporous glasses: (a) glass treated additionally at 700° for 24 h; (b) initial glass not subjected to further heat treatment.

SUPPRESSION OF POLYMER ADSORPTION ON MACROPOROUS GLASSES BY ADDING ADSORPTIVE COMPONENTS TO THE ELUENT

The most important requirement when using macroporous glasses for GPC of polymers is suppression of their adsorption activity, connected with the presence at the surface of active centres, the nature of which is not yet sufficiently clear. With

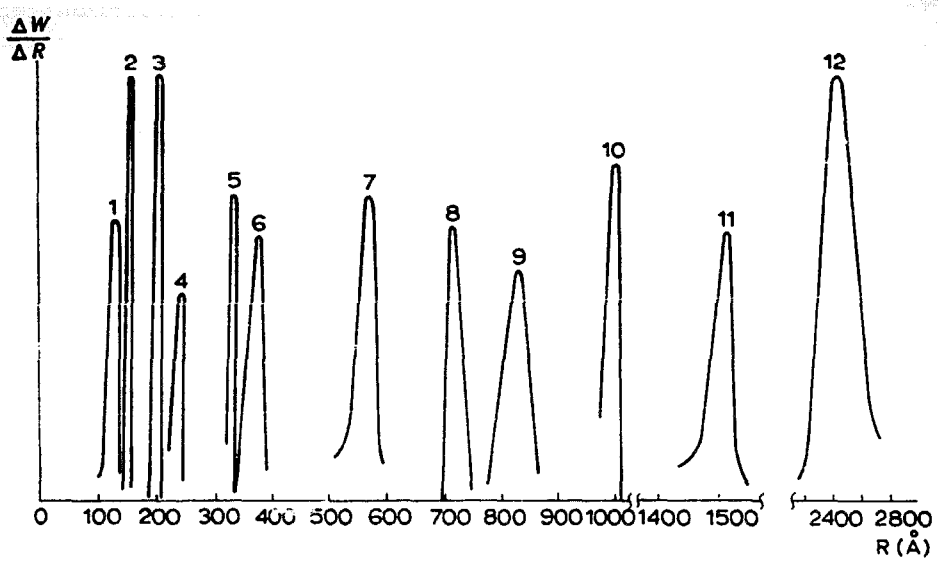

Fig. 2. Curves of pore volume distribution of macroporous glasses *versus* pore size*.

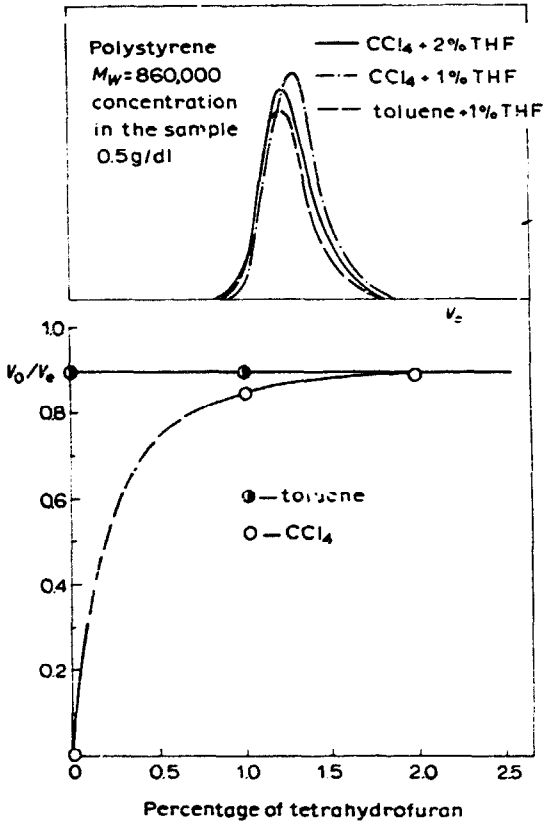

Fig. 3. Influence of additions of tetrahydrofuran on the elution behaviour of polystyrene macromolecules (M_W = 860,000) in tetrachloromethane and toluene.

* Here and further the term "pore size" means the pore diameter.

this aim in view, apart from modifying the surface of porous glass, for example with the aid of hexamethyldisilazane[8,9], the addition of adsorptive components to the eluent can be used. We established by gas chromatography that the adsorption ability of tetrahydrofuran (THF) on porous glasses is forty times higher than that of tetrachloromethane (TCM), and seven times higher than that of toluene. Actually, as can be seen from Fig. 3, when 2 % of THF is added to TCM, the adsorption of polystyrene on the porous glass is suppressed completely, and the elution volume of this polymer in tetrachloromethane coincides with that in toluene. It is clear that the use of pure tetrahydrofuran or dimethylformamide as an eluent enables one to separate, according to the molecular-sieve mechanism on porous glass, even the most polar polymers, for example, polyamido acids (Fig. 4). Hence the appropriate choice of eluent enables the GPC of polymers to be carried out by using a non-modified porous glass. This widens the possibility of utilizing this sorbent in GPC analysis.

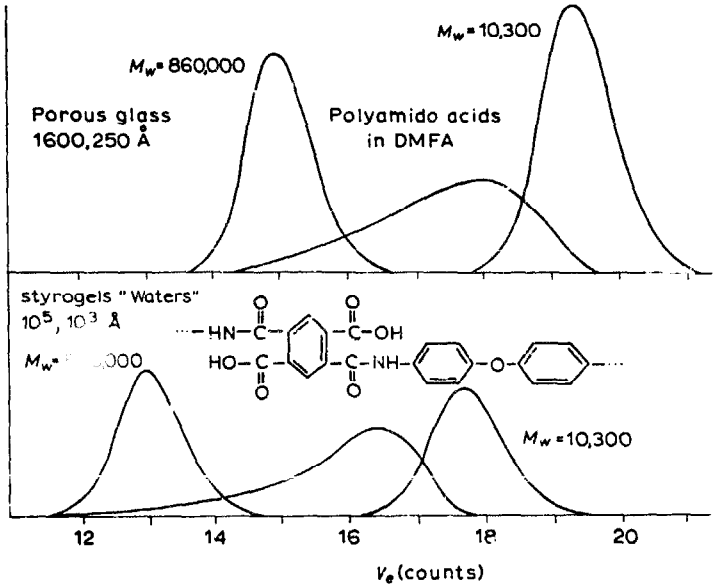

Fig. 4. Comparison of elution behaviour of a sample of polyamido acids with polystyrene standards on porous glasses and styrogels in dimethylformamide.

DEPENDENCE OF ELUTION CHARACTERISTICS ON THE PORE SIZE AND PORE VOLUME OF POROUS GLASS

One of the main chromatographic characteristics of porous glass, as with any other porous sorbent, is the dependence of the elution volume (V_e) on log M, the so-called calibration curve for polymers of a given chemical nature. The calibration curves given by polystyrenes for some samples of macroporous glass differing in pore size are shown in Fig. 5. The mean pore radii are shown on each of the curves. The larger the pore radii of the macroporous glass, the higher is the permeation limit for styrene polymer homologues used for calibration. The free volume, V_0, of the column was determined by using polystyrenes of high molecular weight ($M_W = 25 \cdot 10^6$ and $M_W = 96 \cdot 10^6$) of a narrow distribution ($M_W/M_N < 1.2$) obtained with the aid of

radiation polymerization. The range of the molecular weights for the best separation of such glasses is rather narrow (one decade). However, by joining the columns with porous glasses of different porosity in series, it is possible to widen the range of molecular weights separated by polymers.

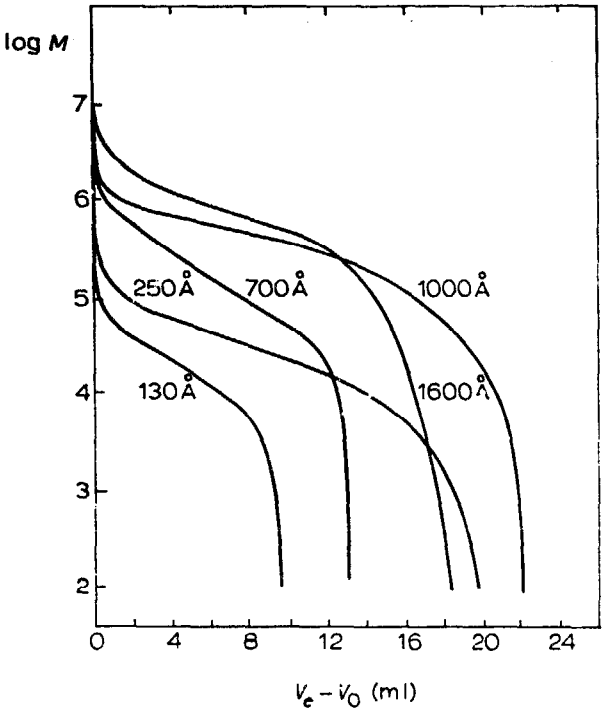

Fig. 5. Plots of $V_e - V_0$ *versus* log M for styrene polymer homologues in toluene for a series of porous glasses with different mean pore size.

Another elution parameter, the dependence of the distribution coefficient, K_d, on log M, where

$$K_d = (V_e - V_0) / (V_{\text{styrene}} - V_0) \qquad (1)$$

was used to study the influence of the grain size of porous glasses prepared under similar conditions on the separation of polymer homologues of styrene in toluene.

Fig. 6 shows the dependence of K_d on log M for various fractions of porous glass of pore size 250 Å. It can be seen that this dependence does not change with changes in the grain size of the sorbent, and consequently, in the character of column packing. It therefore follows that glass grains of different sizes have the same pore structures.

In the molecular-sieve mechanism of separation, the larger the pore volume of a sorbent (V_p) that is accessible to macromolecules, the higher must be the chromatographic resolution of the column. Fig. 7 shows graphs of $(V_e - V_0)$ against log M of polystyrene for porous glasses of pore sizes 250 Å and 1600 Å with different specific pore volumes ($\overline{V}_p$), the values of which are given on the curves. It can be seen from Fig. 7 that the efficiency of the chromatographic separation of polymers with respect

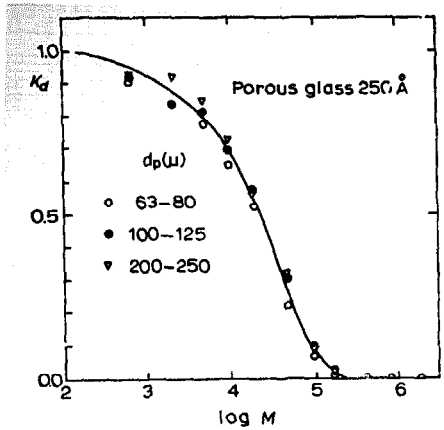

Fig. 6. Influence of the grain size d_p of porous glass of pore size 250 Å on the dependence of the distribution coefficients of polystyrenes on log M.

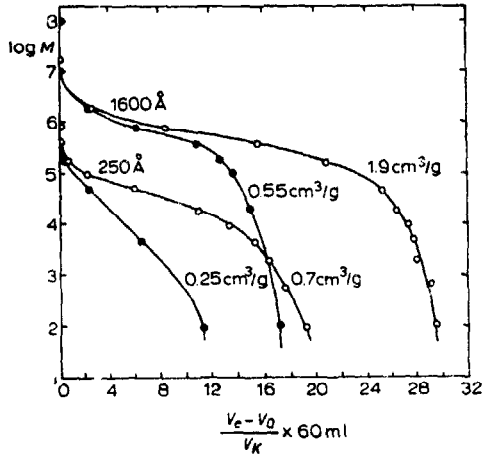

Fig. 7. Influence of the pore volumes of macroporous glass on the separation of styrene polymer homologues on similar columns. (The volume of the columns is 60 ml.)

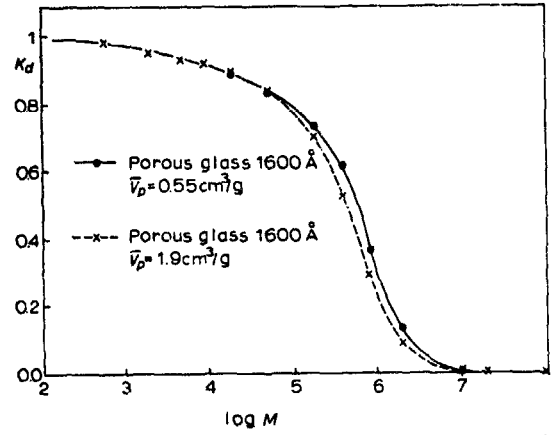

Fig. 8. Plots of K_d *versus* log M of styrene polymer homologous for macroporous glasses of pore size 1600 Å with different pore volumes.

to their molecular weight increases with increasing pore volume of the sorbent, for the same column.

If the distribution coefficient (K_d) is plotted against the logarithm of the molecular weights for two macroporous glasses with the same mean pore sizes but considerably different overall volumes, then, as can seen from Fig. 8, these dependences coincide in both instances. This indicates that, despite the difference in the overall pore volumes, which is nearly as high as a factor of four, the pore geometries of both samples of porous glasses must be similar.

RESOLUTION ABILITY OF CHROMATOGRAPHIC COLUMNS WITH MACROPOROUS GLASSES; COMPARISON OF THEIR EFFICIENCY WITH STYROGEL COLUMN "WATERS"*

The resolution ability of chromatographic columns can be estimated by using the separation coefficient, K_R:

$$K_R = \frac{V_{e2} - V_{e1}}{W_1 + W_2} \tag{2}$$

where W is the width of the chromatographic peak near the base, and the subscripts 1 and 2 refer to the components being separated.

The efficiency of a chromatographic column is expressed by the number of theoretical plates, N, which is related to V_e and W by the following equation:

$$N = 16\left(\frac{V_e}{W}\right)^2 \tag{3}$$

Hence $W = 4V_e/N^{1/2}$. Replacing V_e in eqn. 2 by $V_0 + K_d V_p$ and substituting $K_{d1} - K_{d2} = 2\bar{K}_d$ (where $\bar{K}_d$ is the arithmetical mean of K_{d1} and K_{d2}), we obtain from eqns. 2 and 3:

$$K_R = \frac{\Delta K_d \sqrt{N}}{8\left(\frac{V_0}{V_p} + \bar{K}_d\right)} \tag{4}$$

It can be seen from eqn. 4 that the greater are the efficiency of the column (N) and the ratio V_p/V_0 (*i.e.*, the greater the pore volume of the macroporous glass), the greater is the separation coefficient K_R at given values of ΔK_d and $\bar{K}_d$. On the other hand, at given values of K_R, ΔK_d and $\bar{K}_d$, the increase in the ratio V_p/V_0 enables the number of theoretical plates (N) to be reduced and consequently the column length to be shortened. The latter leads to an increased rate of analysis and enables the overall dimensions of the apparatus to be reduced.

The possibility of preparing porous glasses with different pre-selected porous structures enables one to assemble systems of columns with a linear calibration dependence of V_e on log M for a wide range of molecular weights. Fig. 9 shows such a calibration dependence for systems of columns with two porous glasses (pore sizes 250 Å and 1500 Å), which is linear over a range of molecular weights from $5 \cdot 10^3$ to

* "Waters" = Waters Associates.

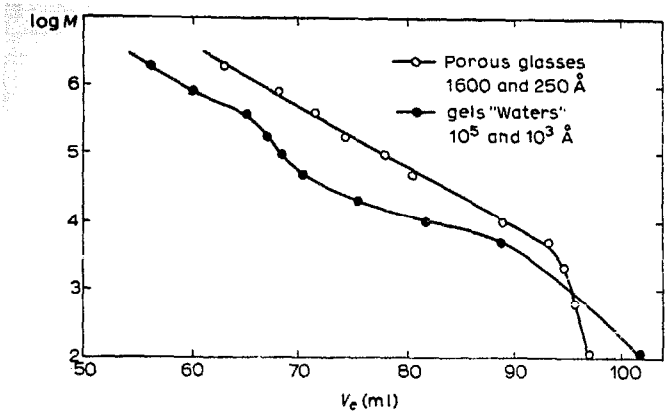

Fig. 9. Calibration curves for systems of two columns: lower, with styrogels "Waters" 10^5 and 10^3 Å, and upper, macroporous glasses (pore sizes 1600 and 250 Å), obtained for styrene polymer homologues in dimethylformamide.

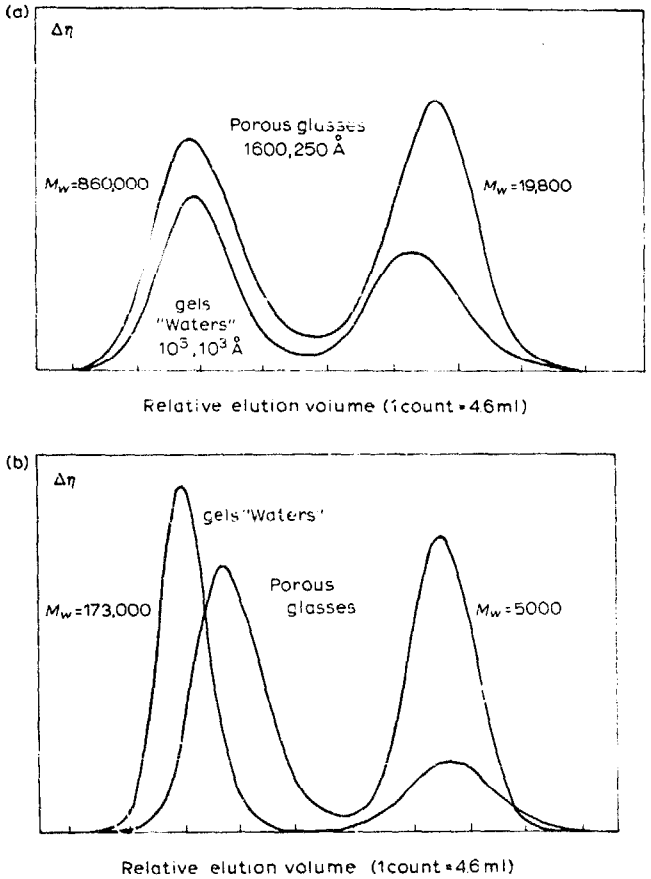

Fig. 10. Comparison of separation of polystyrene standards of (a) M_W = 860,000 and M_W = 19,800 and (b) M_W = 173,000 and M_W = 5000, on styrogel columns "Waters" 10^5 and 10^3 Å and on columns with macroporous glasses (pore sizes 1600 and 250 Å).

$2 \cdot 10^6$. A comparison of this curve with a similar dependence (the lower curve) for two columns "Waters" having permeabilities of 10^5 Å and 10^3 Å reveals that the accessible pore volumes of both systems of columns are similar, and consequently the separation abilities are also similar. Indeed, as can be seen from Fig. 10, both systems show comparable resolutions in the indicated range of molecular weights.

The efficiency of chromatographic columns with porous glass prepared in a special manner not only attains that of columns with styrogels "Waters" but in some instances exceeds it. Fig. 11 shows two chromatograms, the lower of which is the chromatogram of standard polystyrenes with molecular weights of 411,000, 19,800 and styrene obtained on a column 1.2 m in length with styrogel having a permeability of 10^4 Å[10]. The upper one is the chromatogram of polystyrenes with molecular weights of 171,000, 5000 and styrene obtained on a column 0.87 m in length with macroporous glass of pore size 250 Å. It can easily be seen that although the mixture being separated in the column with porous glass is more complex, the separation of high-molecular components is more efficient on this column than on the column of greater length with styrogel "Waters".

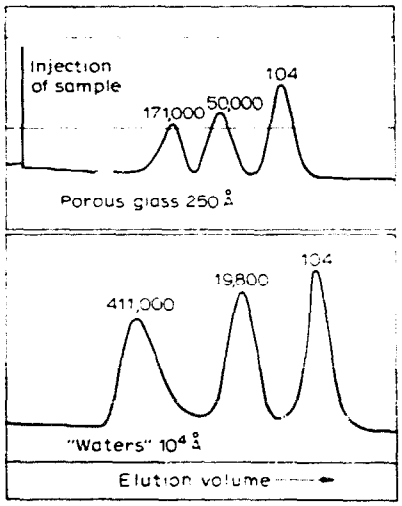

Fig. 11. Comparison of efficiency of separation of polystyrene standards on porous glass (pore size 250 Å) with a grain size of 40–80μ in toluene and on standard styrogel column "Waters" 10^4 Å (see ref. 10).

The results given above indicate convincingly that the use of macroporous glass for the GPC of polymers with the corresponding packing of glass in chromatographic columns enables separation systems to be obtained that give higher resolutions than columns with styrogels.

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