CHROM. 8612

GEL PERMEATION CHROMATOGRAPHY OF POLYMERS ON MACRO-POROUS SILICAS*

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(Received June 16th, 1975)

SUMMARY

   The gel permeation chromatography and adsorption of polystyrenes from different solvents on macroporous silicas (Silochroms) have been investigated, and the adsorption data and chromatographic parameters have been analysed. The influence of the pore diameter on the internal diffusion coefficient macromolecules and the width of the chromatographic peak is shown. The range of applicability of Silochroms to chromatographic fractionation of polymers was determined.

INTRODUCTION

   Under the conditions of gel permeation chromatography (GPC) polymer macromolecules are distributed according to the dimensions of their random statistical coils[1,2]. Non-swelling, rigid, porous adsorbents are sometimes to be preferred over swelling cross-linked organic gels (Sephadex, Sepharose). The accessibility of adsorbent pores to macromolecules of various sizes mainly determines the retention time of these molecules in a column. As was shown by Eltekov and co-workers[3-5], the accessibility of pore volume and internal surface, and the effective coefficients of diffusion of polystyrene macromolecules into the silica gel pores, depend substantially on the adsorbent pore sizes, the pore-size distribution and the temperature. Additionally, the chemical state of the surface of the column packing material has a significant influence in adsorption and chromatographic studies. Undesirable adsorption effects, which distort the character of the macromolecule distribution, may be encountered in GPC conditions on macroporous silicas. These effects can be eliminated by a chemical or adsorption modification of the silica surface[2,6-8].

   This communication presents the results of polystyrene adsorption and GPC on a number of macroporous silicas of different pore sizes, and on chemically modified silica, to estimate the possibility of using these silicas in GPC of polymers, and to determine the correlation between adsorption data and chromatographic parameters.

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* Presented at the 5th Soviet–Italian Chromatography Symposium, Tallinn, April 22–25, 1975.

TABLE I

CHARACTERISTICS OF SILOCHROMS

Sample	Mean pore diameter $(\mathring{A})$	Pore volume, V_s (cm^3/g)	Specific surface, S (m^2/g)
C-1	400	1.1	112
C-2	500	1.3	86
C-3	500	1 2	80
C-4	1100	1.4	45
C-5	1600	1 2	24

EXPERIMENTAL

Materials

Macroporous silicas Silochroms obtained from Aerosil[10] were used as adsorbents and packing material in the chromatographic columns; their characteristics are listed in Table I. The mean diameter and pore volume V_s were determined using a mercury porosimeter. The specific surface areas S of the Silochrom samples were calculated by the BET method from low-temperature nitrogen adsorption data. The column packing was graded from 90 to 160 μm.

Sample C-3 was obtained from Silochrom C-2 by treatment of it with a 20% toluene solution of dimethyldichlorosilane for 48 h at 110°. The sample was then washed with toluene, and dried. Before the experiments, all samples were evacuated at 140° for 6 h.

Narrow fractions of polystyrene (PS) were used, *viz.* the standards of Waters Ass. (Milford, Mass., U.S.A.) with weight-average molecular weights M_w of 10,000, 20,400, 51,000, 97,000, 411,000, 498,000, 860,000, and 1.8×10^6 (polydispersity of PS standards, $M_w/M_n = 1.1$). Two polydisperse polymers, PS-1 and PS-2, with viscosity-average molecular weights $M_\eta = 160,000$ and $M_\eta = 14,000$, were also used. The molecular weights of these two polymers were determined at 20° in benzene using the Mark–Houwink equation with $K = 1.23 \times 10^{-4}$ and $\alpha = 0.72$ (see ref. 9).

Carbon tetrachloride, benzene, toluene, ethylbenzene, and n-heptane were used as solvents.

Adsorption

Adsorption experiments were carried out under static conditions. 4 g of a PS solution of known concentration were poured into an adsorption ampoule with a 0.2-g portion of the dried adsorbent. Ampoules were sealed and stored until adsorption equilibrium was reached, and the equilibrium solution was analyzed by a differential refractometer–interferometer. The amount of adsorption was calculated from the relation[3]:

$$\Gamma = \frac{(C_0 - C)\, m_s}{mS} \tag{1}$$

where C_0 and C are concentrations of the polystyrene solution before and after adsorption, and m and m_s are the masses of adsorbent and solution.

Gel permeation chromatography

GPC experiments were carried out using an XG-1302 Special Construction Bureau Academy of Science (U.S.S.R.) liquid chromatograph with a differential refractometer as detector. The columns, 1200 mm × 8 mm I.D., were dry-packed with Silochrom. The solvent (toluene) flow-rate was 1 ml/min, and 1-ml polymer samples were introduced into the liquid chromatograph at a concentration of 5 mg/ml.

For the parameters of GPC we chose the distribution coefficient K, the height equivalent to a theoretical plate H, the relative height of a theoretical plate h, and the resolution R. Definitions of GPC parameters are listed in Table II.

RESULTS AND DISCUSSION

Fig. 1 shows the isotherms of PS-1 and PS-2 adsorption from dilute solution in carbon tetrachloride and ethylbenzene on Silochroms C-2 and C-3. The figure indicates that modification of the Silochrom surface sharply changes the character of adsorption of polystyrene macromolecules due to a reduction in both the specific and the non-specific (dispersion) interactions between the macromolecules with aromatic rings and the silica surface. The adsorption of polystyrene is changed from positive for hydroxylated Silochrom C-2 to negative for silanized Silochrom C-3. Adsorption of PS-1 and PS-2 from solution in ethylbenzene is negative, which can be attributed to the effect of specific interactions between electron donor molecules of ethylbenzene and protonized silanol groups of the Silochrom surface. The amount of adsorption of PS macromolecules from solution in carbon tetrachloride is about 1 mg/m². We assume these values of adsorption to indicate the adsorption of macromolecules parallel to the surface. According to this simple model, the thickness of the adsorbed layer of polystyrene is about 10–15 Å.

Gel permeation chromatography

Chromatograms of the PS standards and *n*-heptane are characterised by nar-

TABLE II

CHROMATOGRAPHY PARAMETERS

V_t is the elution volume of species i; V_0 is the void volume of a column (the elution volume of the macromolecules not penetrating into the pores): V_t is the total volume of a column (the elution volume of small molecules, *e.g. n*-heptane): W_t is the chromatogram base width of species i. L is the column length; H_0 is the height of the theoretical plate, as found for *n*-heptane.

Parameter	Symbol	Definition
Distribution coefficient	K	$K = \dfrac{V_t - V_0}{V_t - V_0}$
Height equivalent to a theoretical plate (HETP)	H	$H = L\left(\dfrac{W_t}{4\,V_t}\right)^2$
Relative value of height of theoretical plate	h	$h = \dfrac{H_t}{H_0}$
Resolution $(V_t > V_j)$	R	$R = \dfrac{2(V_t - V_j)}{(W_t + W_j)}$
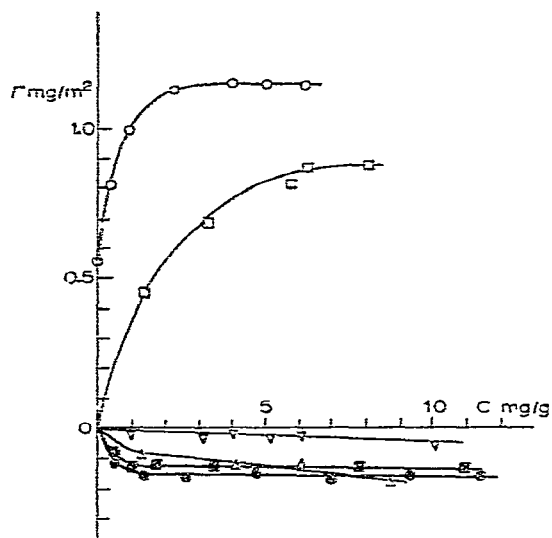
Fig. 1. Adsorption isotherms of PS-1 ($\bigcirc$, $\triangle$, $\oplus$) and PS-2 ($\square$, $\triangledown$, $\blacksquare$) from solutions in carbon tetrachloride ($\bigcirc$, $\square$, $\triangle$, $\triangledown$) and ethylbenzene ($\oplus$, $\blacksquare$) on Silochroms C-2 ($\bigcirc$, $\square$, $\oplus$, $\blacksquare$) and C-3 ($\triangle$, $\triangledown$).

row symmetrical peaks, but chromatographic peaks of the polydisperse samples PS-1 and PS-2 are wide and asymmetrical. Fig. 2 shows logarithmic dependences of the molecular weight of the polystyrene standards as a function of V_i for investigated Silochroms. All the curves display linear parts, almost identical in all cases, and the curves are shifted upwards along the log M_W axis in accordance with pore size (increasing from C-1 to C-5). The difference $V_t — V_0$ corresponds to the pore volume
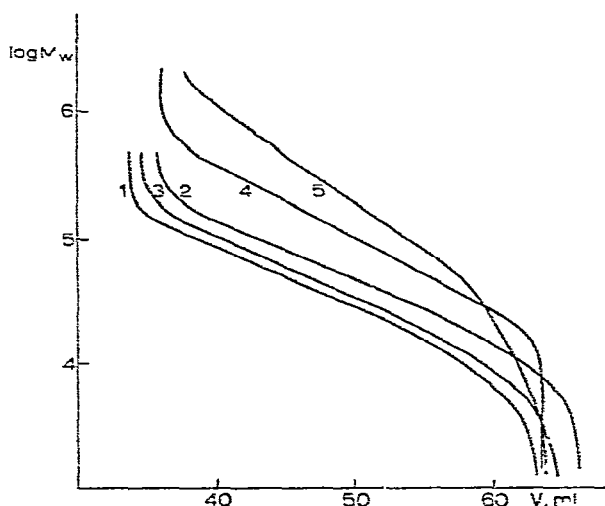

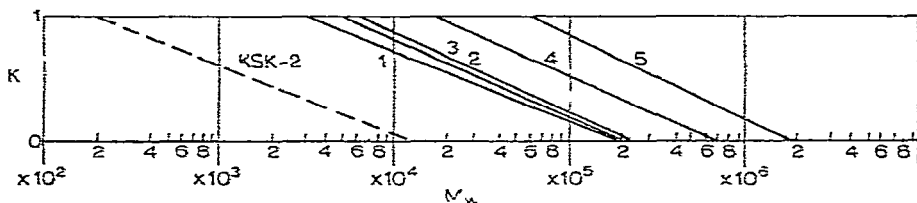Fig. 2. Log M_W as a function of V_i on Silochroms. 1 = C-1; 2 = C-2; 3 = C-3; 4 = C-4; 5 = C-5.

Fig. 3. K as a function of molecular weight of polystyrene for Silochroms. $1 = $ C-1, $2 = $ C-2; $3 = $ C-3; $4 = $ C-4; $5 = $ C-5. KSK-2 $= $ silica gel with mean pore diameter of 140 Å used as standard.

of the packing material, and the values of these differences for the Silochroms are close to values V_s given in Table I. A column filled with a single Silochrom is appropriate for a certain range of molecular weights, as seen in Fig. 3 which gives plots of the distribution coefficient K as function of the molecular weight. Values of K for KSK-2 have been taken from ref. 2. A set of columns, filled with three or four Silochroms, can be used to perform fractionation of polydisperse polymers in a range of M from 10^2 to 10^6.

Fig. 4 shows the dependences of H as a function of log M for PS standards on the investigated silicas. The lowest values of H are observed for Silochrom C-3. The Silochrom modified by silane has a more uniform surface, and leads to a more dense packing of particles in the column due to a removal of electric charge from the surface. The presence of charges on the surface leads to loose packing through electrostatic repulsion between the particles. That the values of H are somewhat higher for samples C-4 and C-5 than for samples C-2 and C-1 is possibly due to their wider pores and associated loose packing of particles in the column. All plots of H as function log M are characterised by a maximum, which arises from a drastic reduction of accessible pores as the dimensions of macromolecule coil increase. The maxima for all species of polymer correspond to values of K in the range 0.1–0.2. If
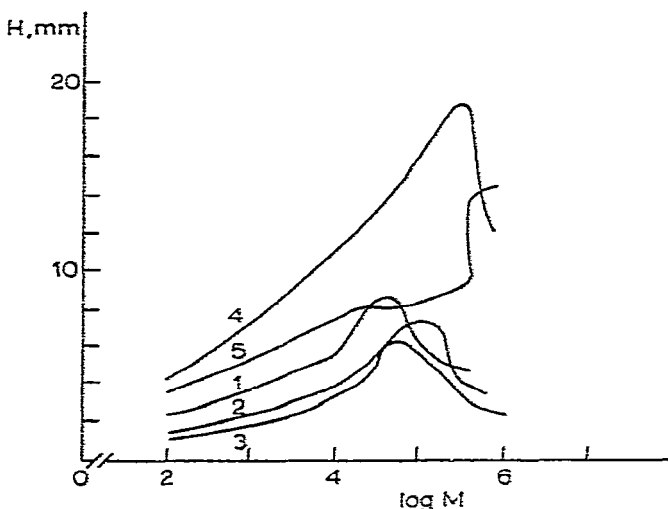

Fig. 4. Dependence of H on log M for narrow fractions of polystyrene on Silochroms. $1 = $ C-1, $2 = $ C-2: $3 = $ C-3; $4 = $ C-4: $5 = $ C-5.
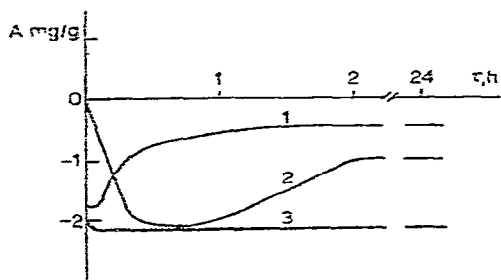
Fig. 5. Diffusion of PS macromolecules with $M_w = 10,000$ (1), 97,000 (2) and 498,000 (3) into pores of Silochrom C-2 at 20°. Solvent, toluene.

coil diameter and pore openings are close to each other, the diffusion coefficient is sharply reduced.

Fig. 5 shows the kinetics of adsorption of a narrow fraction of PS with M_w 10,000, 97,000 and 498,000 from solutions in toluene on sample C-2. The figure indicates that PS from solutions in toluene is adsorbed negatively as compared with solutions in ethylbenzene. At first, molecules of toluene quickly diffuse into the pores of the Silochrom particles, and only then do molecules of PS with M_w 10,000 and 97,000 penetrate displacing molecules of solvent from the pore space. The values of the D-coefficients for effective diffusion of macromolecules into pores may be estimated according to the equation of diffusion of adsorbent into spherical particles[11],

$$D = 0.049\ R^2 \tau_{0.5}^{-1} \tag{2}$$

where R is the radius of Silochrom particle (0.02 cm) and $\tau_{0.5}$ is the time for achieving a value of adsorption equal to half of the equilibrium value.

Due to differences of the r-radii of gyration of macromolecules[12], the rate of diffusion of macromolecules PS with $M_w = 10,000$ ($r = 32$ Å) is higher ($D = 2.5 \cdot 10^{-8}$ cm²/sec) than of PS with $M_w = 97,000$ ($r = 120$ Å, $D = 0.36 \cdot 10^{-8}$ cm²/sec). Macromolecules of PS with $M_w = 498,000$ ($r = 300$ Å) can not penetrate into pores. However, they do not prevent the diffusion of toluene molecules into pores of Silochrom with $r = 500$ Å. The value of the diffusion coefficient for toluene calculated from kinetic data is equal to $D_T = 6 \cdot 10^{-7}$ cm²/sec, as in the presence of macromolecules with $M_w = 97,000$ the diffusion of toluene molecules into pores of Silochrom C-2 is slowed down ($D_T = 3 \cdot 10^{-8}$ cm²/sec).

Table III gives the values of h for n-heptane and the resolution R for two pairs of PS in columns filled with different adsorbents. The data demonstrate that a better separation within the pair of 20,400 and 97,000 PS is achieved on Silochroms with pore diameters from 400–600 Å. This is due to the fact that about 70 % of all the pores are accessible to macromolecules of PS 20,400 and about 20 % to PS 97,000. For Silochroms with pore dimensions in the range 800–1500 Å, the values of K for PS 20,400 and PS 97,000 are close to unity: the pores are almost identically accessible to both polymers, and hence the difference between the K values is less and resolution is poor. The second pair, PS 97,000–411,000 is separated almost identically on all Silochroms.

TABLE III

COMPARISON OF GPC PARAMETERS FOR VARIOUS SILOCHROMS

Sample	M_w	h	R
C-1	20.400	3.0	
	97.000	2.7	1.02
	411.000	2.1	0.53
C-2	20.400	2.7	
	97.000	4.5	0.94
	411.000	2.2	0 76
C-3	20.400	3.4	
	97.200	4.7	1.1
	411.000	2.5	0.59
C-4	20.400	3.0	
	97.200	3.9	0 43
	411.000	4.6	0.52
C-5	20.400	2.2	
	97.200	2.2	0 30
	411.000	2 6	0.48

The values of h are close to each other for all the Silochroms; however, as expected, the values are smaller for Silochroms with the maximum pores. This could be explained by the pores of Silochrom C-5 being almost identically accessible to molecules of toluene and macromolecules of PS, except PS with $M_w = 411,000$, for which h is higher, and the coefficient of effective diffusion smaller. The highest values of h for each Silochrom are observed in the case where the dimensions of the macromolecule coil and pore are closest; the smallest when the macromolecule coil easily penetrates into pores or does not penetrate at all.

Thus, the analysis of the values of h allows us to obtain valuable information on the correlation between the molecular weight of a polymer and the pore sizes of the packing material.

ACKNOWLEDGEMENTS

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