Journal of Chromatography, 168 (1979) 234–240

CHROM. 11,230

Note

Thin-layer gel-permeation chromatography of polymers on a porous glass bead support

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(Received June 5th, 1978)

The possibility of effecting separations of polymers by thin-layer gel-permeation chromatography (TLGPC), based on the molecular sieve mechanism, has been reported by several workers[1–6]. All of this previous work was carried out on silica gel or modified silica gel supports. In the work reported here, however, separations were carried out on a porous glass bead support. Also presented is the correlation of the results from TLGPC with those from normal column GPC. As in previous work[3,7], adsorption effects are suppressed, if not eliminated, by pre-eluting, *i.e.*, pre-equilibrating, the plates before addition of the sample.

EXPERIMENTAL

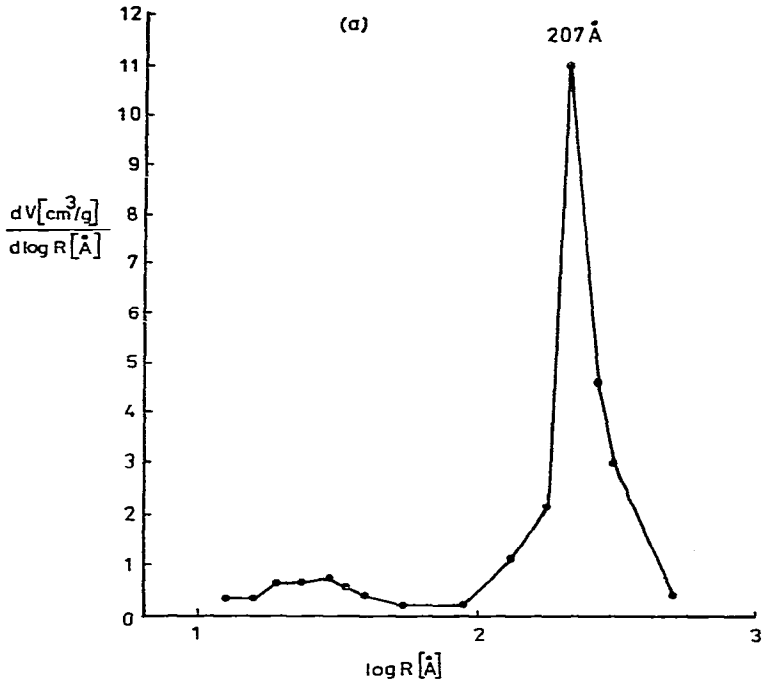
Materials

Siliconized porous glass beads (bead size 15–35 μm) produced in the Department of Physical Chemistry of this University, using the procedures of Dawidowicz and co-workers[8–12], were used as the stationary phase (support). The pore size distribution, for this gel, was determined by using a Sorptomat 1806 (Carlo Erba, Milan, Italy). The distribution curve obtained, plus the adsorption-desorption isotherms, are shown in Fig. 1a and b.

As can be seen from Fig. 1a, the effective pore diameter is 207 Å. Narrow-distribution polystyrene standards ($M_w/M_n < 1.1$, obtained from Waters Assoc., Milford, Mass., U.S.A.), with the designations and nominal molecular weights given in Table I, were used as the samples. For the determination of the K_d values of the column (these values, although they show a straight-line relationship with the R_s values, are not presented here), *o*-dichlorobenzene (ODCB) was used. Chloroform (chemically pure, obtained from POCH, Gliwice, Poland) was used as the solvent.

Method

The gel was slurried with the solvent and this slurry was applied to the plates (20 × 12 × 0.4 cm) to a thickness of 1 mm. The plates were then immediately transferred into the closed-vessel development apparatus, being held in the sandwich device designed by Soczewiński[13]. The plates were equilibrated overnight before addition of the sample. For this work, descending development was used. The solvent was



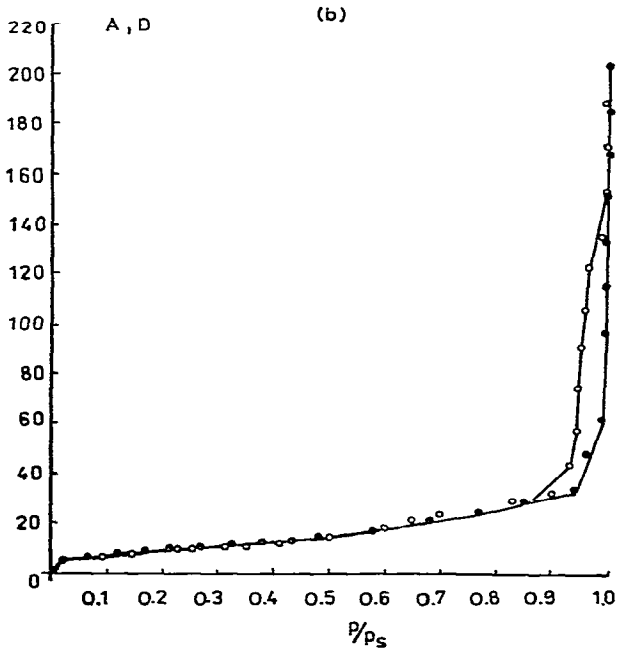


Fig. 1. (a) Pore size distribution curve and (b) adsorption–desorption isotherms for siliconized porous glass beads. V = pore volume; R = pore radius; (●) adsorption; (○) desorption.

TABLE I

DESIGNATION, MOLECULAR WEIGHTS AND PEAK MAXIMA OF SAMPLES

Code	*Mol. wt.**	*Peak maximum (Å)*
PS1	2100	49.5
PS2	3600	86.9
PS3	8000	193.2
PS4	20,800	500
PS5	33,000	841
PS6	111,000	2707
PS7	200,000	4700
PS8	390,000	9024
PS9	670,000	15,975
PS10	2,610,000	56,097
PS11	3,700,000	67,000
ODCB	147.01	3.5

* As obtained from Waters Assoc.

led to the plate by means of a wick made of Whatman No. 4 chromatographic paper; the excess of the solvent was collected by a second wick, which permitted evaporation of the solvent and hence continuous development of the plates was achieved. This procedure is very similar to the method of development devised by Morris[7]. The angle of inclination to the horizontal was 20°. The samples (8 μl of a 0.5% w/v solution in chloroform) were applied as spots using a 10-μl Hamilton 701 syringe.

After a running time of 1 h, the development was stopped and the plates were dried in air. The polymer spots were located by exposure to UV light for 30 min; the common staining processes[2–6] cannot be used, because the gel is siliconized with tetramethylchlorosilane, which reacts with the staining materials.

Fig. 2 shows the results of a typical run and Table II gives the R_s values, plus

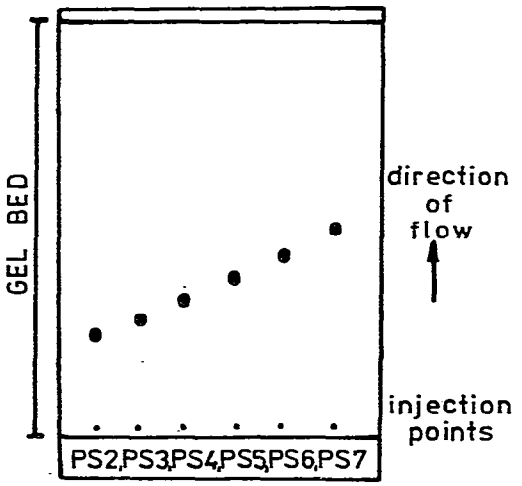


Fig. 2. A typical plate run. Time, 1 h.

TABLE II

R_s VALUES AND DISTANCE OF MIGRATION (d_m) FOR THE 15–35 μm GEL–CHLOROFORM SYSTEM

Polymer code	R_s	d_m *(cm)*
PS1	0.70	5.00
PS2	0.76	5.35
PS3	0.83	5.85
PS4	0.92	6.50
PS5*	1.00	7.05
PS6	1.09	7.65
PS7	1.16	8.00
PS8**	—	—
PS9**	—	—
PS10**	—	—
PS11**	—	—

* Polymer PS5 is used as the standard, *i.e.*, $R_s = 1$.
** R_s and d_m values could not be measured.

the average distances travelled (d_m), for the TLGPC runs; R_s is defined as the ratio of the distance travelled by a sample (d_m) to the distance travelled by polymer sample 5 (d_{m5}), *i.e.*, $R_s = d_m/d_{m5}$.

Column chromatography

A stainless-steel column (100 × 0.4 cm I.D.) was packed, using a dry packing method, with the gel and 10-μl portions of sample solution of the same concentration as above were introduced by means of a Waters U6K injector. The solvent was delivered with an Orlita AE 10/4 pump at a flow-rate of 1.24 ml/min. The column effluent was monitored at 254 nm with a Varian Aerograph Model 0.21428:03 instrument. The recorder speed was 1 cm/min at a deflection of 1 mV.

RESULTS AND DISCUSSION

By using the parameter K_f introduced by Donkai and Inagaki[4], the data from the plates and column can be correlated; K_f is defined as the ratio of two overall migration rates and by the equations

$$K_f = (d_m/t)/(d_{m7}/t) = d_m/d_{m7} \quad (1)$$

for the plate, where d_m is as defined above, d_{m7} is the distance travelled by polymer 7 (this polymer exceeds the permeation limit of the gel) and t is the time interval, and

$$K_f = (1/V_e)/(1/V_ei) = V_ei/V_e \quad (2)$$

for the column, where V_ei is equal to the interstitial volume, *i.e.*, for polymers whose molecular weights exceed the permeation limit of the gel, and V_e is the elution volume (in ml). V_e is calculated from the equation

$$V_e = (30/x)z \quad (3)$$

TABLE III

K_f VALUES FOR THE THIN-LAYER AND COLUMN SYSTEMS

Polymer code	$^{11}K_{fc}$*	$^{7}K_{fp}$*
PS1	0.723	0.625
PS2	0.728	0.670
PS3	0.774	0.730
PS4	0.795	0.812
PS5	0.832	0.881
PS6	0.933	0.955
PS7	0.972	1.000
PS8	0.997	—
PS9	1.000	—
PS10	1.000	—
PS11	1.000	—
ODCB	0.688	—

* For the column K_f values are given with respect to PS11 and for the plate with respect to PS7 (both exceed the permeability limit of the gel).

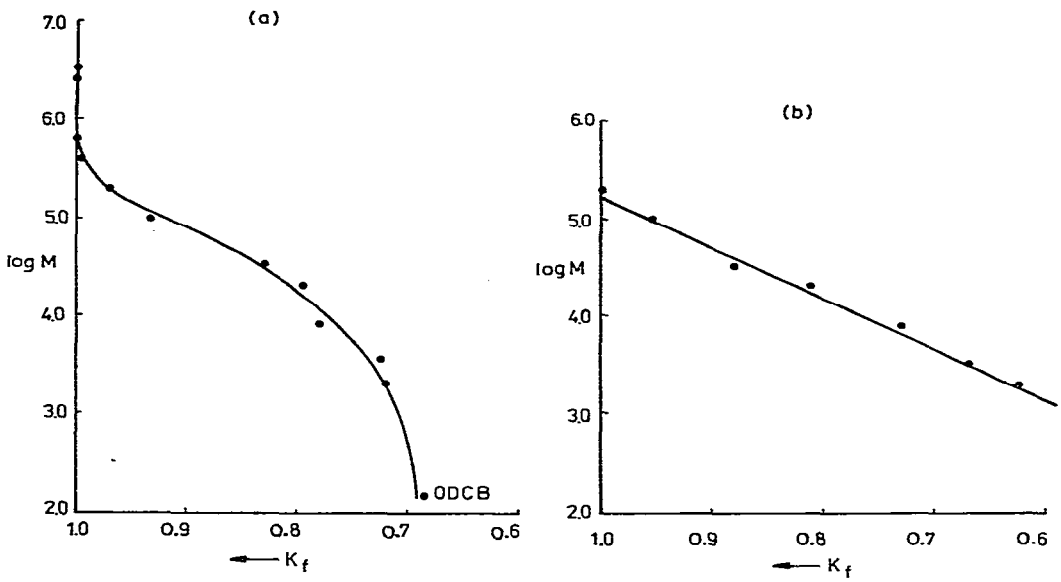


Fig. 3. (a) Plot of $^{11}K_f$ (column) for the 13–35 μm gel–chloroform system. PS1–PS11 + ODSB. (b) Plot of $^{7}K_f$ (plate) for the 15–35 μm gel–chloroform system. PS1–PS7.

where x is the time (in sec) in which 0.5 ml of solvent is eluted from the column and z is the distance to the peak maximum from the point of injection (in mm). Values of K_f for the plate and the column are presented in Table III and Fig. 3a and b.

The V_e and V_s values for the column are given in Table IV; V_s is equivalent to V_e with respect to polymer 5, for which $V_s = 1$.

A graph of the V_s and R_s values, taken from Tables II and IV, against the molecular weights of the polymer samples is shown in Fig. 4.

TABLE IV

V_e AND V_s VALUES FOR THE COLUMN

Polymer code	V_e	V_s
PS1	9.990	0.869
PS2	9.928	0.875
PS3	9.336	0.930
PS4	9.087	0.956
PS5	8.687	1.000
PS6	7.750	1.121
PS7	7.438	1.168
PS8	7.246	1.199
PS9	7.2	1.215
PS10	7.2	1.215
PS11	7.2	1.215
ODCB	10.497	0.828

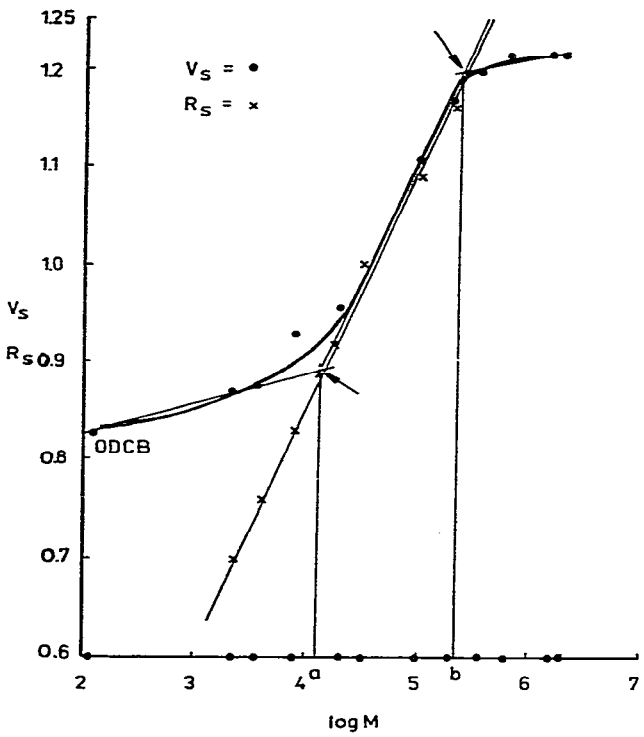


Fig. 4. Plots of V_s (column) and R_s (plate) parameters. Data taken from Tables II and IV. $a = \log 4.08 = 12{,}000$; $b = \log 5.4 = 250{,}000$.

From Figs. 3 and 4, it can be seen that for this gel the thin-layer system gives a better separation of polymers whose molecular weights are less than 12,000. For the range between 12,000 and 250,000, the thin-layer system gave separations comparable to, if not slightly better than, the column system. Unfortunately, molecular weights

above 250,000 could not be investigated because of the occurrence of diffusion effects resulting from the high masses involved. It can be deduced from these figures that with this gel the molecular weight limits in column work are 12,000–250,000.

The observation that the thin-layer system is comparable to the column system within these limits, and better outside these limits, contradicts previous results.

The method of performing TLGPC as proposed by Donkai and Inagaki[4], *i.e.*, pre-eluting the plate to a distance of about 10 cm before addition of the sample, and not equilibrating overnight, did not give satisfactory results.

REFERENCES

1 B. G. Belinkii and E. S. Gankina, *Dokl. Akad. Nauk SSSR*, 186 (1969) 520.
2 B. G. Belinkii and E. S. Gankina, *J. Chromatogr.*, 53 (1970) 3.
3 B. G. Belinkii and E. S. Gankina, *J. Chromatogr.*, 141 (1977) 13.
4 H. Donkai and H. Inagaki, *J. Chromatogr.*, 71 (1972) 473.
5 E. P. Otocka, M. Y. Helman and P. H. Muglia, *Macromolecules*, 5 (1972) 227.
6 H. Halpaap and K. Klatyk, *J. Chromatogr.*, 33 (1968) 80.
7 C. J. O. R. Morris, *J. Chromatogr.*, 16 (1964) 167.
8 A. Waksmundzki, Z. Suprynowicz, J. Gawzik and A. Dawidowicz, *Chem. Anal. (Warsaw)*, 19 (1974) 1033.
9 A. Dawidowicz, A. Waksmundzki and Z. Suprynowicz, *Chem. Anal. (Warsaw)*, 21 (1976) 917.
10 A. Dawidowicz, B. Ościk and A. Waksmundzki, *Chem. Anal. (Warsaw)*, 22 (1977) 1155.
11 A. Waksmundzki, A. Dawidowicz, S. Sokołowski and M. Jaroniec, *Chromatographia*, 8 (1975) 234
12 A. Dawidowicz, A. Waksmundzki and S. Sokołowski, *Separ. Sci.*, 12 (1977) 573.
13 E. Soczewiński, *J. Chromatogr.*, 138 (1977) 443.