

THE MOLECULAR WEIGHT DEPENDENCE OF THE SPREADING FACTOR OF SEC COLUMNS AND THE SURFACE STRUCTURE OF THE PORE OF PACKINGS

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ABSTRACT

The molecular weight separation and column dispersion for a number of SEC columns packed with various packing materials were calibrated simultaneously using narrow MWD polystyrene standards as probe. The molecular weight dependence of the spreading factor is closely related to the surface structure in the pore of packings.

Size exclusion chromatography (SEC) is widely used for the characterization of molecular weight distribution (MWD) of polymers, but it needs a prior calibration by means of polymer standards with known average molecular weights or MWD^[1]. The calibration curve for molecular weight separation of SEC is a direct reflection of the porosity and pore size distribution of the porous packings^[2,3]. According to this fact and the mechanism of separation of SEC, a method has been proposed recently in the literature^[4-7] for determining the porosity and pore size distribution of porous material by experimental technique of SEC with narrow MWD polymer standards as probe. In the course of SEC separation, the diffusion of macromolecules inside the pore certainly should be influenced by the internal surface structure of the pore and reflected on the chromatographic behaviors. It will be inferred that some information about the interior pore surface structure probably may be obtained from the experimental chromatograms of monodispersed polymers, i.e. the spreading functions. The investigation about this problem is scarce in the literature both in experimental and theoretical. An important reason is that the determination of the spreading function or its eigenvalue, i.e. spreading factor is a difficult task since there are no truly monodispersed polymer standards exist in fact and the contribution of the polydispersity to the experimental chromatogram of narrow MWD polymer standards is nonnegligible. With the aid of the theoretical relationship between the calibration function of a SEC column for the monodispersed polymer species under ideal working condition and the effective relations between the molecular weight and elution volume^[8], a method for simultaneous calibration of molecular weight separation and column dispersion was proposed^[9]. Therefore a means for investigating the influence of the porous structure of SEC packing on the spreading factor is provided.

For the organic and inorganic porous packings of SEC, porous crosslinked polystyrene gel and porous silica beads are most widely being used nowadays. The common feature of

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these materials is that all of them have permanent pores, but the surface structure inside the pore is different because both the chemical composition and method of preparation are not identical. The results of electron microscopic observation^[10] indicates that the interior surface of the pore wall of crosslinked polystyrene gel is very rough and that of porous silica beads is relatively smooth. These facts are also reflected in the results of specific surface area determination of the dry gel. The specific surface area of crosslinked polystyrene gel with various pore sizes all are around several tens to hundreds square meters per gram dry gel while that of silica beads decreases rapidly with increasing pore size and goes down to a few even less than 1 square meter per gram for silica beads with large pore. In this laboratory two sorts of SEC packings namely porous ethylvinylbenzene-divinylbenzene gels^[11] and porous silica beads^[12] had been prepared. These packings were characterized by measuring their bulk density, skeleton density, specific surface area S , specific pore volume v_p , porosity ψ , average pore diameter $\bar{D}$, exclusion limit $M_{\max}$ and the effective pore volume fraction V_p of the packed column. The measured results of the typical packings are listed in Table 1. The average pore diameter of the porous packings are calculated from the experimental v_p and S data as

$$\bar{D} = 4 \cdot 10^4 \cdot v_p / S \quad (\text{\AA})$$

for penetrating cylindrical pore model. It is likely that the discrepancy between the estimated value and the real value of pore diameter are quite large due to the complexity in the structure of skeleton and pore surface of the porous packings. Comparing the crosslinked polystyrene gel with large pore size to the silica beads with similar exclusion limit, the average diameter of

Table 1 Characteristics of the typical porous SEC packings

Porous packing	Exclusion limit $M_{\max}$, PS	S (M^2/g)	v_p (ml/g)	$\bar{D}$ ($\text{\AA}$)	ψ	V_p
Silica Beads						
000	$3.2 \cdot 10^4$	273	1.05	150	0.69	0.41
500	$3 \cdot 10^5$	132	1.01	300	0.69	0.41
600	$2 \cdot 10^6$	19	1.04	2200	0.69	0.43
650	$1 \cdot 10^6$	15.4	1.03	2600	0.69	0.41
700	$6 \cdot 10^6$	10.0	0.95	3800	0.67	0.40
730	$2 \cdot 10^7$	3.9	0.73	7400	0.62	0.34
Crosslinked polystyrene gel						
40—48	$9 \cdot 10^3$	124	0.31	100	0.27	0.12
40—39	$1.5 \cdot 10^5$	125	0.52	170	0.37	0.18
40—32	$6 \cdot 10^5$	130	0.85	260	0.47	0.25
40—24	$2 \cdot 10^6$	132	1.16	350	0.56	0.31
40—16	$5 \cdot 10^6$	67	1.81	1100	0.66	0.36

the latter is about ten fold larger than the former. Since the interior surface of the pore of crosslinked polystyrene gel is very rough and having a large surface area, the penetrating cylindrical model implicates an assumption of smooth pore wall surface, so that leads to a smaller estimated average pore diameter.

It is easy to understand the reason of the porous crosslinked polystyrene gel has a rough pore surface from the mechanism of permanent pore formation^[14]. As styrene or ethylvinylbenzene copolymerizes with divinylbenzene the network structure of the copolymer skeleton is in homogeneous due to divinylbenzene has faster rate of polymerization. The interior surface of the permanent pore formed as a consequence of phase separation of the copolymer in the presence of diluent certainly consists of appropriate amount of polystyrene free chain ends with proper length attached on the crosslinked skeleton. In the dry state the free chain ends coil up and result in a rough pore wall surface with increased surface area. When it is immersed in a solvent the crosslinked skeleton swells to a limited extent by absorption a definite amount of solvent while the free chain ends after swelling may move inside the region of a semisphere with a radius approximately equal to the extended length of the free chain end. The free chain ends extending from the pore wall somewhat like the hairs in naval cavity (even though the volume occupied by them inside the pore is small), their action could not be neglected and the chromatographic process certainly should be influenced by them. When the solute molecule diffuses into or out of the pore and comes into collision with the free chain ends, its movement should be restricted and going by a roundabout route requires more time. It is conceivable that this restriction effect should increase with increasing molecular weight of the solute and be controlled by the amount and length of the extending free chain ends. The spreading function or the numerical value of spreading factor of monodispersed polymer in a SEC column is related to the extent of restricted diffusion, so the difference in pore surface structure of the packings ought to be reflected on the molecular weight dependency of spreading factor. It may be expected that such dependency should be more pronounced for the crosslinked polystyrene gel as a result of the interior pore surface is much more coarse than that of silica beads.

For testing and verifying the above inference we took a series of narrow MWD polystyrene standards characterized by GPC-LALLS coupling technique^[15] as common probe to calibrate simultaneously the separation and spreading effect^[9] of a number of SEC columns packed with crosslinked polystyrene gel and silica beads. The results of spreading factors σ_0^2 obtained are listed in Table 2. Because the volume of the column and syphon tube are different for each SEC unit, the experimental data of spreading factor can not be compared directly. If the relative spreading factor, i.e. the ratio of spreading factor to that with least molecular weight (A1) are taking into account, its variation with molecular weight of probe is shown in Fig. 1. The results conform completely with the inference. The molecular weight of polystyrene standard varies from $4 \cdot 10^3$ to $3 \cdot 10^6$ and covers three orders of magnitude. The modes of variations of relative spreading factors have distinct difference between these two types of packings. For the porous silica beads with smooth pore wall surface the relative spreading factors merely increased a few folds at the most and coincided with each other for different SEC units. The relative spreading factors for crosslinked polystyrene gel with rough pore wall surface are much more larger showing up a remarkable molecular weight dependence and distinguishable for different column units. It indicates that the surface structure

characterized by the amount and length of free chain ends of various packed crosslinked polystyrene gel from different sources are nonidentical due to their conditions of polymerization are not the same.

Table 2 Molecular weight dependence of spreading factor of conventional SEC column

Polystyrene probe		Spreading factor, σ_0^2				Relative spreading factor, $\sigma_0^2/\sigma_0^2(A1)$			
PS	$\langle M \rangle_w \times 10^{-4}$	Silica beads		Crosslinked PS gel		Silica beads		Crosslinked PS gel	
		1	2	3	4	1	2	3	4
A1	0.4	13.4	1.14	0.14	0.74	1	1	1	1
A2	1.0	14.0	0.95	2.77	2.05	1.04	0.83	19.3	2.77
A3	2.04	16.2	—	—	2.85	1.21	—	—	3.85
A4	11	15.3	1.50	2.50	4.33	1.14	1.32	17.9	5.85
A5	39	16.3	1.71	3.10	4.07	1.22	1.50	22.1	5.50
A6	286	34.0	3.79	4.95	7.66	2.53	3.32	35.4	10.4

1. Silica beads, ARL 950 GPC, THF.
2. Silica beads, Home-made SEC unit, toluene.
3. Crosslinked polystyrene gel, ARL 950 GPC, THF.
4. Crosslinked polystyrene gel, Home-made SEC unit, toluene.

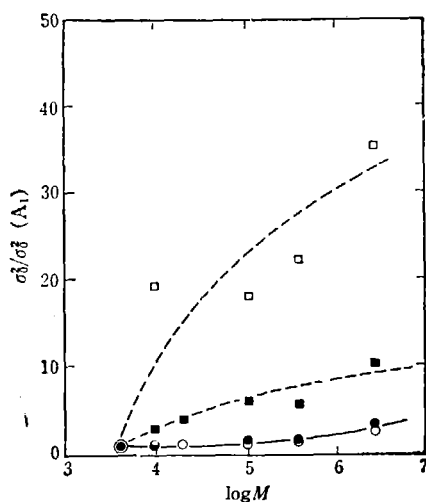


Fig. 1 Molecular weight dependence of the relative spreading factor of conventional SEC columns

- Columns 1 and 2, Silica beads;
 □■ Columns 3 and 4, Crosslinked polystyrene gel.

The experimental results shown in Table 2 and Fig. 1 are obtained in conventional SEC columns with packings of usual size. For further understanding the influence of polymerization condition and pore surface structure on the spreading factor, the same polystyrene standards were used as probe to determine the spreading factor of two sets of high performance SEC columns (Waters 150C- μ -Styragel and Waters 244-Shodex). The results obtained are listed in Table 3 and the variation of the relative spreading factor with the molecular weight of probe is shown in Fig. 2. It can be seen from Fig. 2 that the spreading factor of HPSEC column

Table 3 Molecular weight dependence of spreading factor of HPSEC columns with microparticulate crosslinked polystyrene gel packings

Polystyrene probe		Spreading factor, σ_0^2		Relative spreading factor, $\sigma_0^2/\sigma_0^2(A1)$	
PS	$\langle M \rangle_w \times 10^{-4}$	μ -Styragel	Shodex	μ -Styragel	Shodex
A1	0.4	0.044	0.029	1	1
A2	1.0	0.053	0.015	1.20	0.52
A3	2.04	0.083	0.045	1.88	1.55
A4	11	0.139	0.068	3.14	2.34
A5	39	0.228	0.073	5.16	2.51
A6	286	1.81	0.80	41.0	27.6

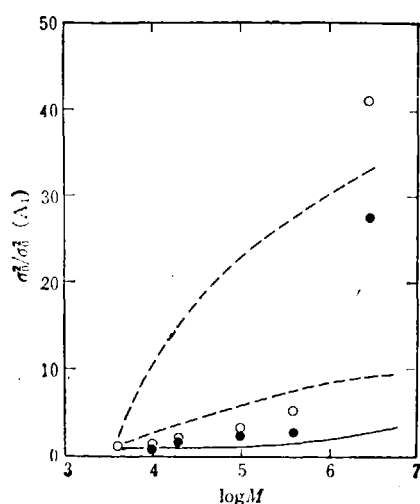


Fig. 2 Molecular weight dependence of relative spreading factor of HPSEC column with microparticulate packings

- μ -Styragel; ● Shodex A80M;
- Conventional column with silica beads;
- Conventional column with crosslinked polystyrene gel.

packed with microparticulate crosslinked polystyrene gel also increases with increasing molecular weight of probe but has its own feature. As the molecular weight of probe $M < 10^5$ the relative spreading factor is less than that of crosslinked polystyrene gel with conventional particle size though still greater than that of silica beads. As the molecular weight of probe $M > 10^5$, the relative spreading factor increases abruptly to an extent similar to that of conventional crosslinked polystyrene packings. This fact shows that the pore wall surface of microparticulate packing is more smooth than that of conventional packing, the length of their free chain ends are shorter and the high molecular weight polymers are more sensitive to it. Such a characteristic of the microparticulate packing is presumably resulted from the high degree of crosslinking of the gel skeleton, i.e. probably due to the amount of the monofunctional monomer in the copolymerization mixture is relatively small.

EXPERIMENTAL

Characterization of porous packings

The bulk density, skeleton density and swelling ratio were determined by weighing tube method, specific pore volume v_p and solvent regain of the dry gel were determined by titration method, exclusion limit of the packing was estimated from the calibration curve of the packed column, the porosity of the packing ψ and the effective pore volume fraction of the column V_p were calculated from above data. The details of the experimental method had been described in previous papers^[13,14].

Polystyrene standards

Six ARL narrow MWD polystyrene standards were used as probe, their inhomogeneity indexes had been characterized by coupling SEC-LALLS method^[15].

Size exclusion chromatography

SEC experiments were carried on an ARL 950 GPC instrument and a number of home-made SEC units for columns packed with conventional sized porous packings. All of the elution volume were counted by siphon tube with tetrahydrofuran or toluene as eluent.

Experiments with microparticulate packings were carried on a Waters 150C and a Waters 244 HPSEC instruments. The former contained three μ -Styragel columns (10^6 , 10^5 , and 10^4 Å) and the later contained a Shodex A80M column. Tetrahydrofuran was used as eluent for both cases, maintaining a flow rate of 1 ml per minute and elution time was counted. The method of data treatment is the same as described previously^[9]. The calibration curves of conventional SEC columns could be well represented by a linear function but that of HPSEC should be represented by a polynomial as shown in Fig. 3.

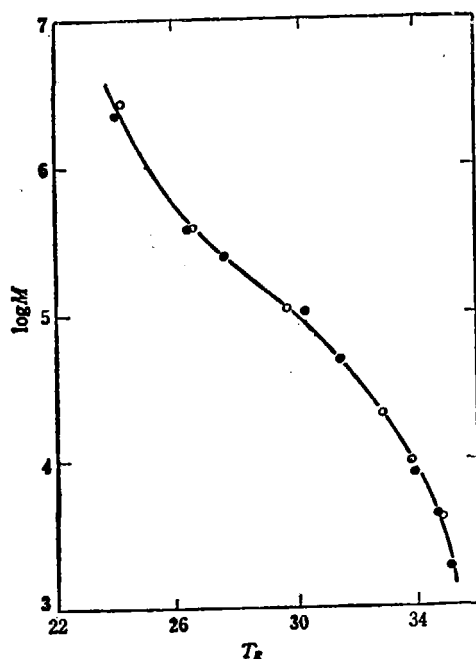


Fig. 3 Calibration curve of HPSEC column packed with μ -Styragel

○ ARL PS standards;
● Waters PS standards.

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