

Study on Resolution Capacity and Secondary Mechanisms of Three Different TSK Gels for Organic SEC

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Abstract

A comparative study on the elution behavior in size-exclusion chromatography (SEC) of three polymeric TSK gel packings, named H, H_{HR}, and H_{XL} types, is performed. The deviations of the universal calibration (u.c.) curves of seven solvent–polymer systems show evidence that the existence of secondary effects accompanying the main SEC mechanism. These secondary mechanisms are a consequence of the binary enthalpic interactions between the different components of the chromatographic system, such as polymer–solvent, polymer–gel and solvent–gel. However, in the present case, the observed deviations from a unique u.c. curve can mainly be attributed to adsorption of polymeric solutes (analytes) onto the residual moieties of the gel surfaces, (i.e., to polymer–gel interactions). These enthalpic interactions can be quantitated by the values of the distribution coefficient, K_p , which follows the order: $K_p(\text{gel H}_{XL}) > K_p(\text{gel H}_{HR}) > K_p(\text{gel H})$. Moreover, the specific resolution of the three types of packings is also estimated, and its comparison yields that $R_{sp}(\text{gel H}_{HR}) > R_{sp}(\text{gel H}_{XL}) > R_{sp}(\text{gel H})$, in good agreement with their increasing particle size and decreasing crosslinking degrees. Finally, the errors and inaccuracies committed on the estimation of the sample average molar masses from their respective calibration curves serves the assessment that the packing with lesser secondary mechanisms is the H-type.

Introduction

Size-exclusion liquid chromatography (SEC) is a powerful and widely used analytical technique for polymer characterization in organic or aqueous eluents (1–14). The main separation mechanism in SEC is driven by size; that is, by entropic effects. In the literature, recent studies on separation models (15) and on adsorption effects (16) can be found but systematic analysis on the response of SEC columns are scarce (17). In this sense, previous and recent research by our group (18–25) has analyzed the

swelling and crosslinking degrees of gels based on crosslinked polystyrene (PS)–divinylbenzene (DVB) copolymer, such as μ -styrigel, TSK gel H_{HR}, and TSK gel H_{XL}. Moreover, the partition coefficient (K_p), fractal dimension, concentration effects, and preferential solvation parameter were also determined for many solvent–polymer systems by means of the SEC technique. The analysis of the values of these variables has served the discussion and explanation of the secondary effects that accompany the main size-exclusion separation process. Chromatographically speaking, the secondary mechanisms have been shown through the shifts from a single universal calibration (u.c.) curve, as proposed by Benoit et al. (26,27).

The main purpose of the present study is to perform a comparative and exhaustive analysis of the SEC elution behavior of different types of PS–DVB packings. In this regard, at present, Tosohaas, one of the first manufacturer of SEC columns, can provide three complete sets of TSK-type supports named TSK gel H (the older developed packing) and the current and more sophisticated TSK gels H_{HR} and H_{XL}. Our previous knowledge of some properties in the elution behavior of two of them (20–25) has prompted us to extend the study to the H-type columns on one hand, and to include new solvent–polymer systems on the other. Moreover, another goal of the present work is to relate the cross-linking degree (ν), distribution coefficient (K_p), and specific resolution (R_{sp}), with the secondary effects observed in the u.c. curves, which are mainly caused by solute-reversible adsorption onto the residual moieties on the gel surface.

Experimental

Chemicals

Narrow standard polymer samples of polybutadiene (PBD) (Polymer Source Inc., Dorval, Canada), polydimethylsiloxane (PDMS) (Polymer Laboratories, Shropshire, U.K., and Polymer Source Inc., Dorval, Canada), polystyrene (PS) and polymethylmethacrylate (PMMA) (Pressure Chemical, Pittsburgh, PA) have

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been used in the present work. The weight average molar masses (M_w) and polydispersity index of the samples used with the different packings are compiled in Table I.

Chromatographic-grade solvents, namely, tetrahydrofuran (THF), 1,4-dioxane (DIOX), benzene (BZ), toluene (TOL), and cyclohexane (CHX) from Scharlau (Barcelona, Spain) were used as eluents.

Chromatography

The Waters liquid chromatography equipment with a refrac-

Table I. Weight Average Molar Masses of the Narrow Standard Polymers Used for SEC Measurements in TSK Gel Packings

M_w (g/mol)			
PS	PBD	PDMS	PMMA
4000 ^{*,†,‡}	920 [†]	1140 ^{†,‡}	5780 ^{*,†}
6870 ^{*,†,‡}	5950 [*]	8100 ^{*,†,‡}	9200 [‡]
17,200 ^{*,†,‡}	6250 ^{†,‡}	33,500 ^{†,‡}	26,900 ^{*,†,‡}
30,000 ^{*,†,‡}	12,600 ^{†,‡}	41,500 [*]	70,500 ^{*,†,‡}
42,300 ^{*,†,‡}	13,400 [*]	76,030 [*]	160,500 ^{*,†,‡}
90,000 ^{*,†,‡}	34,000 [†]	123,000 ^{†,‡}	254,000 [†]
114,000 ^{*,†,‡}	42,300 [‡]	188,000 ^{†,‡}	257,200 [‡]
200,000 ^{*,†,‡}	47,000 [*]	188,400 [*]	550,000 ^{*,†,‡}
355,000 ^{*,†,‡}	60,700 ^{†,‡}	681,600 [*]	
400,000 ^{*,†,‡}	67,300 [*]		
650,000 ^{*,†}	86,500 [*]		
706,000 [‡]	94,250 [*]		
1,432,000 ^{*,†,‡}	105,700 ^{†,‡}		
2,700,000 ^{*,†,‡}	268,000 [*]		
3,800,000 ^{*,†,‡}	323,000 ^{†,‡}		
6,590,000 ^{*,†,‡}	360,000 ^{†,‡}		
	1,120,000 [*]		

* Used in TSK gel HHR.
† Used in TSK gel HXL.
‡ Used in TSK gel H.
§ Polydispersity index: PS (1.05–1.10), PBD (1.03–1.15), PDMS (1.03–1.23), and PMMA (1.03–1.15).

tive index detector (Waters, Milford, MA) used for SEC experiments has been previously described (28). The coupled column sets used were two sets of three TSK gel H_{HHR} and TSK gel H_{HXL} columns in series (each one of 7.8- × 300-mm i.d.) and one set of three TSK gel H columns (each one of 7.5- × 300-mm i.d.) from Tosohaas, Tosoh Corp. (Tokyo, Japan). Some of their packing properties such as particle size; nominal pore size; pore, total-exclusion, and total-permeation volumes (V_p , V_0 , and V_T , respectively); and molar mass separation range are listed in Table II.

All the solvents used as eluents were previously degassed and filtered by passing them under vacuum through 0.45- μ m regenerated cellulose filters from Micro Filtration Systems (Dublin, CA). All chromatographic experiments were performed at 25.0°C in a thermostated heater, and the columns were equilibrated overnight prior to starting any experiment. Chromatograms were obtained at a flow rate of 1.0 mL/min by injecting 100 μ L of sample solutions. To avoid concentration effects (29), all solute samples were injected at four concentrations, and elution volumes were determined by extrapolating to zero concentration. The elution behavior was expressed as universal calibration plots, which were linear in the molar range studied here ($r \geq 0.998$).

Viscometric measurements

The intrinsic viscosity $[\eta]$ is related to the polymer molar mass (M) through the Mark-Howink-Sakurada (MHS) equation: $[\eta] = kM^\alpha$. The exponent α from this equation represents the thermodynamic quality of the solvent by the polymer. The intrinsic viscosities of the samples were determined from specific viscosities measurements at 25.0°C, as previously described (20). The obtained MHS parameters k and α are listed in Table III.

Results and Discussion

In "ideal" SEC, the separation of macromolecules is accomplished by size, and the concept of universal calibration proposed by Benoit et al. (26,27) is fulfilled. In this context, the sample

Table II. Column Packing Characteristics

Commercial	Gel packing	Pore size name	Particle size (μ m)	Effective M_w range*	V_0 (mL) [†]	V_T (mL) [‡]	V_p (mL)
TSK gel HHR	Crosslinked PS-DVB copolymer	G2500	5	200–40,000	16.40	33.2	16.8
		G4000		1000–60,000			
		G6000		10,000–4,000,000			
TSK gel HXL	Crosslinked PS-DVB copolymer	G2500	5	200–40,000	17.07	33.7	16.7
		G4000		1000–500,000			
		G6000		10,000–2,000,000			
TSK gel H	Crosslinked PS-DVB copolymer	G2500	13	< 20,000	15.46	30.35	14.9
		G4000		< 400,000			
		G6000		< 40,000,000			

* Approximate ranges and exclusion limits given by the manufacturer.
† As determined with a PS standard of high molar mass ($M_w = 6,590,000$ Da).
‡ Determined with small solutes, TOL, or BZ, in THF as the eluent.

elution volume is related to their hydrodynamic volume by the well-known equation:

$$\log M[\eta] = a + bV_e \quad \text{Eq. 1}$$

in which the product $M[\eta]$ represents the hydrodynamic volume (V_h) of the solute and a and b are the corresponding linear fitting coefficients. However, in "real" conditions, interactions between the components of the chromatographic system take place, and the u.c. method expressed by equation 1 no longer holds. As a consequence of secondary elution mechanisms, deviations from a single curve account for the solvent-polymer systems being eluted (30–37). In general, the shifts of the calibration curves from a reference depend on the type and strength of the interactions between solvent, solute, and gel (19–21). For these cases of nonideal SEC, the elution volumes are given by:

$$V_e = V_0 + K_D V_p \quad \text{Eq. 2}$$

where V_0 is the interstitial or void volume of the column, V_p is the pore volume, and K_D is a global distribution coefficient equal to the ratio of solute concentration in the stationary phase and in the mobile phase. Therefore, K_D accounts both for size-exclusion and for secondary effects and may be written as (38):

$$K_D = K_{SEC} K_p \quad \text{Eq. 3}$$

where K_p and K_{SEC} are the partition and the distribution coefficient by size, respectively. Because K_{SEC} is only based on entropic interactions, it can be thermodynamically expressed by (38):

$$K_{SEC} = \exp(\Delta S/R) \quad \text{Eq. 4}$$

This coefficient reflects the change in conformational entropy when the macromolecular solute is transferred from the mobile phase to inside the pores. Because the conformational degrees are more restricted inside the pores, the conformational entropy decreases, $\Delta S < 0$ and $K_{SEC} < 1$.

On the other hand, the interactions of polymeric solute with the pore walls result in a change in enthalpy and, accordingly, the distribution coefficient accounting for solute-gel interactions or secondary effects may be written as (38):

Table III. Mark-Howink-Sakurada Coefficients for Diverse Solvent-Polymer Systems at 25.0°C

System	k (mL/g)	μ
THF-PBD	0.0109	0.760
BZ-PBD	0.1120	0.604
DIOX-PBD	0.1550	0.541
BZ-PDMS	0.0579	0.572
TOL-PDMS	0.0447	0.601
CHX-PDMS	0.1590	0.534
THF-PS	0.0110	0.725
THF-PMMA	0.0075	0.720
DIOX-PMMA	0.0114	0.714

$$K_p = \exp(-\Delta H/RT) \quad \text{Eq. 5}$$

Therefore, if solute-gel interactions are repulsive, $\Delta H > 0$ and $K_p < 1$, whereas if interactions are of attractive nature (as reversible adsorption of polymer onto the gel surface), $\Delta H < 0$ and $K_p > 1$.

Figures 1–3 show the calibration plots, as $\log M[\eta]$ versus V_e of seven solvent-polymer systems eluted in TSK gel H, gel H_{HR}, and

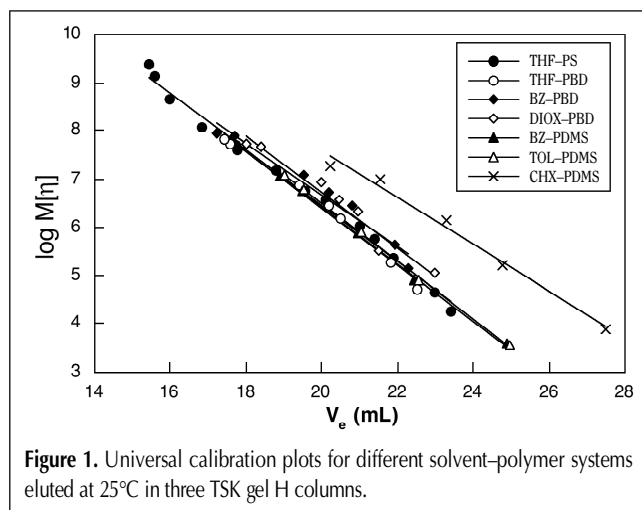


Figure 1. Universal calibration plots for different solvent-polymer systems eluted at 25°C in three TSK gel H columns.

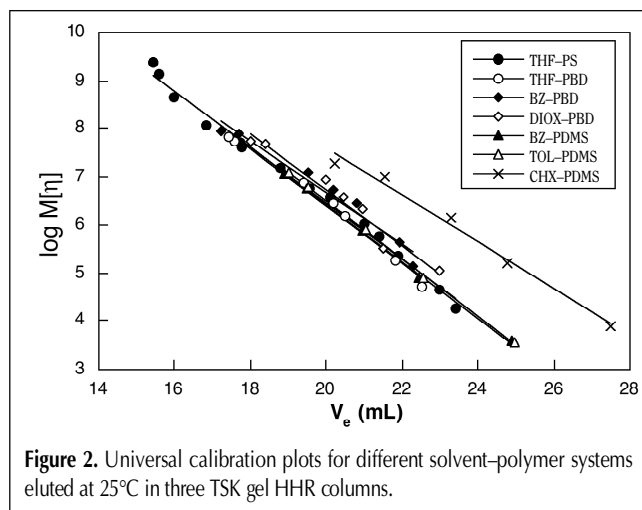


Figure 2. Universal calibration plots for different solvent-polymer systems eluted at 25°C in three TSK gel HHR columns.

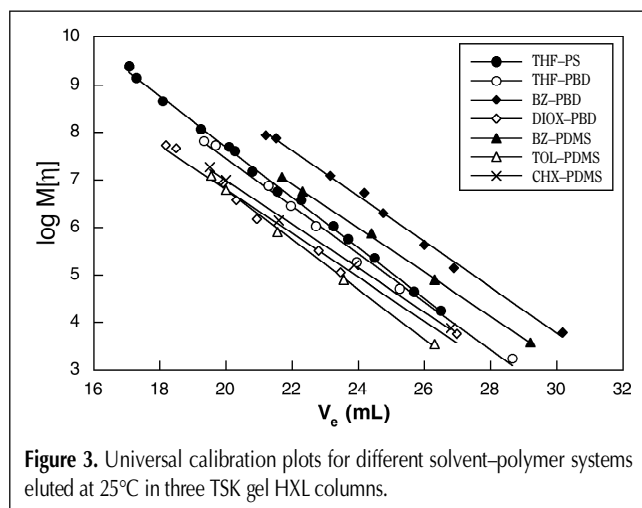


Figure 3. Universal calibration plots for different solvent-polymer systems eluted at 25°C in three TSK gel HXL columns.

gel H_{XL}, respectively. As can be seen, two main features deserve to be mentioned and commented on. In the first place, deviations from the reference THF–PS curve are observed in general, especially for the H_{HR} and H_{XL} gels, and follow the order: gel H < gel H_{HR} < gel H_{XL}. Generally it is assumed that secondary effects are absent in the THF–PS system. Henceforth, it may be taken as a reference system for which the universal calibration holds. Second, it is remarkable that the CHX–PDMS system displays different relative positions with respect to the reference in the diverse gels. Both points can be related to the interactions between the solutes and moieties on the gel surfaces caused by the gel synthesis procedure. The synthesis of the crosslinked PS–DVB copolymer constituent of the packings is usually carried out through suspension polymerization processes. The drop-let stabilizers (surfactants) used in these processes greatly vary: from poly(vinylalcohol), poly(vinylpyrrolidone), methyl cellulose, gelatin, and gums up to inorganic salts such as calcium sulphate, calcium phosphate, and benzonite. Porogens are also used to control the pore size, being that they are frequently used saturated aliphatic carboxylic acids of variable chain length. It should be noted that most of what was mentioned also applies if the packings are made by emulsion polymerization, which rarely occurs in commercial practice. Therefore, a great variety of different moieties can remain on the packing pore surface. Moreover, it is likely that different surface groups will vary from one manufacturer to another and even from one to another packing type of the same manufacturer. The differences on elution behavior for a given solvent–polymer system among the diverse PS–DVB columns may be not solely (or mainly) attributable to differences in the crosslinking degree but also to the enthalpic interactions between remnant surface groups and polymeric solute. Accordingly, different K_p values should be obtained for the same solvent–polymer systems eluted in different gels.

The classical research of Benoit et al. on universal calibration demonstrated that a large variety of polymers (linear and star-shaped), as well as copolymers, follow a single calibration curve (26,27). In this pioneering work it is clear that in the PS–DVB gels used, the particle size was higher and the crosslinking degree smaller than in current ones, so no solute–gel interactions were accounted. However, in modern gels, as Figures 1–3 show, a unique curve is not obtained because sometimes the curves of the diverse systems are far apart from the reference. The origin of the differences between Benoit and our results, as pointed out before, is probably attributable to the preparation methods of modern gels. These methods allow for reduced particle size and, consequently, achievement of a tighter packing with a reduction of the dead volume (~ 10%), as the comparison between current (20–22,24,25) and approximately 25-year old (39,40) columns shows. Moreover, the pore volume of actual columns is approximately twice that of the old ones, yielding a better separation of polymeric solutes. In fact, the newer columns display a light increase on the specific resolution but, unfortunately, much larger K_p values.

The separation efficiency of a column is usually given by its resolution (R_s), which expresses the column capacity to separate the polymeric solutes 1 and 2 with respective molar masses M₁ and M₂, and is defined as:

$$R_s = \frac{2(V_2 - V_1)}{w_1 + w_2} \quad \text{Eq. 6}$$

where V₁ and V₂ are the retention volumes of solutes 1 and 2, and w₁ and w₂ are the widths of the chromatographic peaks of species 1 and 2 at the baseline. The defined resolution depends on the polydispersities of the two samples. This drawback can be overcome by defining a new parameter, the specific resolution R_{sp} as (41):

$$R_{sp} = \frac{2(V_2 - V_1)}{[w_1 I_1 + w_2 I_2] \log \frac{M_{w,2}}{M_{w,1}}} \quad \text{Eq. 7}$$

where I_i is the polydispersity index ($I_i = \frac{M_{w,i}}{M_{n,i}}$) of samples

i (i = 1,2) with weight average molar mass (M_{w,i}) and number average molar mass (M_{n,i}). Therefore, R_{sp} measures the separation efficiency of the column and is directly related to the theoretical plates number (N). Consequently, the higher the R_{sp} value, the higher the N value and the better the column packing resolution. The values of the magnitudes needed to evaluate R_{sp} of the three column sets assayed are listed in Table IV and the corresponding R_{sp} data in Table V. An inspection of these data reveals that the efficiency order is R_{sp} (TSK gel H_{HR}) > R_{sp} (TSK gel H_{XL}) > R_{sp} (TSK gel H), in agreement with their V_p values. Then, the maximum efficiency (or better performance) is obtained for the gel with lower particle size and higher crosslinking degree, the TSK gel H_{HR}.

On the other hand, the quantitative determination of K_p has been conducted for three hydrodynamic volume values, namely V_h = M[η] = 10⁶, 10⁷, and 10⁸ mL/mol. Previously to K_p calculations, it was necessary to evaluate the K_{SEC} coefficients for the column sets at each V_h. In the present work, the TOL–PDMS system has been chosen as the reference because it is generally the system with lowest retention volumes. For this reason, K_p = 1, and the application of equations 2 and 3 to the reference system yields:

$$V_e = V_0 + K_{SEC} V_p \quad \text{Eq. 8}$$

from which K_{SEC} can be estimated at the hydrodynamic volumes selected by taking V₀ and V_p data from Table II and V_e from the fitting of the TOL–PDMS calibration curve according to equation 1. Afterward, the K_p values can be obtained from equations 2 and 3 for each solvent–polymer system assayed in the three sets of TSK columns. These values are also listed in Table V and follow, in general, the trend: K_p (gel H_{XL}) > K_p (gel H_{HR}) > K_p (gel H), in good accordance with the experimental elution behavior shown in Figures 1–3. The higher K_p values for the modern TSK H_{XL} gel denotes that, in this packing, stronger solute–gel interactions occur. However, a contradiction arises in respect to the old TSK gel H set because, on one hand, their R_{sp} values are the smallest, as expected from their largest particle size, but on the other, the K_p values are also the smallest. This fact indicates that the old H-type gel displays lesser secondary effects than the modern ones; that is, a greater universality for separation purposes in spite of its lower specific

resolution. Let us now approach this matter from a different viewpoint, such as is the determination of sample average molar masses from the SEC calibration curves.

Usually, the calibration of a column set is made by eluting PS standards in THF according to equation 1, in which the intrinsic viscosities $[\eta]$ are quantitated through the MHS equation $[\eta] = kM^\alpha$. By substituting the MHS equation in equation 1, and after some rearrangements a particular calibration for PS in THF is obtained:

$$\log M_w = \frac{a - \log k}{1 + \alpha} + \frac{b}{1 + \alpha} V_e = A + B V_e \quad \text{Eq. 9}$$

where a, b, A, and B are the fitting coefficients of the calibration curves. Assuming that the u.c. is fulfilled, the previous expression can be generalized to any solvent-polymer system with their own MHS coefficients k' and α' (42):

$$\log M_w = \frac{a - \log k'}{1 + \alpha'} + \frac{b}{1 + \alpha'} V_e = A' + B' V_e \quad \text{Eq. 10}$$

Equation 10 allows for the evaluation of the average molar mass of any polymer sample from its chromatogram in the corresponding eluent. However, if the calibration curve $\log M_w[\eta]$ versus V_e for a polymer in a given solvent differs from the reference u.c. (THF-PS)—that is, obeys the equation $\log M[\eta] = a' + b' V_e$ —the particular calibration for that system will be given by:

$$\log M_w = \frac{a' - \log k'}{1 + \alpha'} + \frac{b'}{1 + \alpha'} V_e = A'' + B'' V_e \quad \text{Eq. 11}$$

with a' , b' , A'' and B'' being the corresponding fitting parameters. Therefore, it is evident that the larger the deviation between the M_w value evaluated from equation 11 and the nominal value given by the supplier, the larger the shift between the particular calibration and the u.c.; or in other words, the larger the K_p values with respect to the reference system. In this sense, Table VI shows the nominal and calculated M_w data together with the mathematical deviations between both sets of values for diverse solvent-polymer systems eluted in the three column sets. Deviation (DEV) is defined as the relative difference between nominal and calculated M_w values and is expressed as a percent by:

$$DEV = \frac{|M_w(nom) - M_w(cal)|}{M_w(nom)} \times 100 \quad \text{Eq. 12}$$

As a general rule, quantitative deviation follows the order TSK gel H < TSK gel H_{HR} < TSK gel H_{XL}, with mean deviations of 21%, 49%, and 121%, respectively. Moreover, uncertainties of approximately the same order are also found when comparing the molar masses of a solute in a particular solvent in the diverse column sets. As expected, the order in M_w deviation was similar to the one followed by the K_p values given in Table V because smaller K_p values indicate closer M_w values to those deduced from u.c., and they also agree with the experimental evidence given in Figures 1–3. However, it could be argued that DEV values listed in Table VI have been obtained with the classical THF-PS reference system, whereas the K_p values were deduced in respect to the TOL-PDMS. For this reason, calculations on

Table IV. Data for the Specific Resolution Calculations of the Column Sets through Equation 7

Column Set	Rsp variables	Solvent-polymer system*			
		BZ-PBD 6000	BZ-PDMS 8000	TOL-PDMS 8000	
TSK gel H	$V_{e,1}$ (mL)	22.6	22.4	22.4	1.5
	w_1 (mL)	1.2	2.0	1.8	
	$V_{e,2}$ (mL)	20.7	20.9	21.0	
	w_2 (mL)	1.4	1.7	1.7	
TSK gel HHR	$V_{e,1}$ (mL)	22.8	22.6	22.75	
	w_1 (mL)	1.3	1.8	1.9	
	$V_{e,2}$ (mL)	20.45	20.75	20.7	
	w_2 (mL)	1.3	1.3	1.3	
TSK gel HHR	$V_{e,1}$ (mL)	23.1	23.0	23.0	
	w_1 (mL)	1.7	2.6	2.2	
	$V_{e,2}$ (mL)	20.8	21.0	21.1	
	w_2 (mL)	1.3	1.4	1.1	

* BZ-PBD 6000: $M_{w,1} = 6250$ Da; $M_{n,1} = 6000$ Da; $M_{w,2} = 42300$ Da, and $M_{n,2} = 41,000$ Da.
 BZ-PDMS 8000: $M_{w,1} = 8100$ Da; $M_{n,1} = 7500$ Da; $M_{w,2} = 33,500$ Da; and $M_{n,2} = 316,000$ Da.
 TOL-PDMS 8000: $M_{w,1} = 8100$ Da; $M_{n,1} = 7500$ Da; $M_{w,2} = 33,500$ Da; and $M_{n,2} = 316,000$ Da.

Table V. Specific Resolutions and Distribution Coefficients at Three Hydrodynamic Volumes (in mL/mol), for the TSK Column Sets in Diverse Solvent-Polymer Systems

Column set	Solvent-polymer system	R_{sp}	K_p			
			$V_h = 10^6$	$V_h = 10^7$	$V_h = 10^8$	
TSK gel H	THF-PBD	1.69	0.96	0.94	0.89	
	BZ-PBD		1.08	1.06	1.00	
	DIOX-PBD		1.11	1.12	1.14	
	BZ-PDMS		1.56	0.98	0.96	0.90
	TOL-PDMS		1.28	1.00	1.00	1.00
TSK gel HHR	THF-PBD	2.10	0.98	0.97	0.94	
	BZ-PBD		1.21	1.16	1.04	
	DIOX-PBD		1.27	1.36	1.66	
	BZ-PDMS		1.80	1.25	1.24	1.25
	TOL-PDMS		1.94	1.10	1.10	1.11
TSK gel HXL	THF-PBD	1.78	1.31	1.52	3.01	
	BZ-PBD		1.88	2.47	6.72	
	DIOX-PBD		1.06	1.00	0.63	
	BZ-PDMS		1.51	1.56	1.89	4.26
	TOL-PDMS		1.74	1.00	1.01	1.00

molar masses and deviation have been repeated by taking the TOL–PDMS system as a reference u.c. The corresponding values are also compiled in Table VI in parenthesis. On one hand, they confirm the general trend observed for the diverse types of columns, and on the other, the proper choice of the alternative TOL–PDMS as reference system (at least in the packings studied here) because the deviations are even lower than those obtained with the classical THF–PS system.

Conclusion

The present work analyzes the elution behavior of three types of SEC packings commercialized by Tosohaas. All of them are separate solutes in the same range of sizes, but they have different particle sizes and crosslinking degrees.

The separation strength has been compared through the values of their specific resolution (R_{sp}). As expected, the TSK gel

H_{HR} columns display the largest R_{sp} values because they possess the higher crosslinking degree and pore volume.

In contrast, the smaller shifts between the calibration curves in respect to the reference have been observed in the columns with the largest particle sizes (H-type), denoting lower solute–gel interactions, which is more adequate for sample characterization purposes. This experimental evidence has been corroborated by the values of K_p , which is the coefficient that quantitatively accounts for secondary mechanisms and follows the order: $K_p(\text{gel } H_{XL}) > K_p(\text{gel } H_{HR}) > K_p(\text{gel } H)$.

Finally, the excellence of the packings for sample characterization has been judged through the estimation of the errors or uncertainties committed when determining the average molar masses through the corresponding calibration curves. Again, the gel with lowest deviation has turned out to be the H-type. Therefore it is necessary to achieve a compromise between decreasing particle size, increasing crosslinking degree, and improving the separation efficiency in the synthesis of modern gels. This matter is rather complicated because the current gel

synthesis procedures increase the number of moieties on the gel surface, which can interact with polymeric solutes and decrease other important properties of SEC gels (such as their effective resolution) to the detriment of a proper evaluation of molar masses and molar-mass-distribution functions of unknown samples.

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Table VI. Relative Deviation (DEV) between Nominal and Evaluated Weight Average Molar Masses of Diverse Polymeric Solutes in TSK Gel Columns

Column set	Eluent–polymer system	Nominal M_w	Evaluated M_w	DEV (%)	%Mean DEV
TSK gel H	THF–PS	42,300	37,200 (39,100)	12 (8)	21 (21)*
	THF–PMMA	70,500	67,000 (72,100)	5 (2)	
	DIOX–PMMA	70,500	46,700 (50,400)	34 (29)	
	THF–PBD	42,300	37,200 (39,800)	12 (6)	
	THF–PBD	60,700	55,200 (60,600)	9 (0)	
	BZ–PBD	12,600	8900 (9100)	29 (28)	
	BZ–PBD	60,700	39,200 (44,100)	35 (27)	
	TOL–PDMS	8100	10,200 (10,000)	26 (24)	
	TOL–PDMS	33,500	36,600 (47,600)	9 (42)	
	BZ–PDMS	33,500	42,200 (45,200)	26 (35)	
	BZ–PDMS	8100	11,000 (10,800)	36 (33)	
TSK gel H_{HR}	THF–PBD	47,000	144,400 (85,800)	143 (83)	49 (47)*
	THF–PBD	67,300	140,600 (108,000)	109 (61)	
	BZ–PBD	47,000	43,500 (29,300)	7 (38)	
	DIOX–PBD	47,000	37,800 (23,800)	20 (49)	
	DIOX–PBD	67,300	50,700 (33,100)	25 (51)	
	CHX–PDMS	41,470	27,300 (16,400)	34 (61)	
	CHX–PDMS	76,035	45,300 (29,000)	40 (62)	
	BZ–PDMS	41,470	39,800 (24,000)	4 (42)	
	BZ–PDMS	8100	8100 (3900)	0 (52)	
	TOL–PDMS	41,470	65,000 (42,900)	57 (3)	
	TOL–PDMS	8100	16,300 (8900)	101 (10)	
TSK gel HXL	THF–PMMA	70,500	75,400 (23,100)	7 (67)	121 (64)*
	THF–PBD	34,000	48,200 (15,200)	42 (55)	
	BZ–PBD	34,000	6700 (1900)	80 (94)	
	BZ–PBD	12,600	2600 (780)	79 (94)	
	BZ–PDMS	33,500	19,100 (5300)	43 (84)	
	BZ–PDMS	123,000	89,000 (24,200)	28 (80)	
	TOL–PDMS	33,500	166,200 (46,100)	396 (38)	
	TOL–PDMS	8100	31,900 (9000)	294 (1)	

* Values in parenthesis are in reference to the TOL–PDMS reference system.

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