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Evaluation of the porous structures of new polymer packing materials by inverse size-exclusion chromatography

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Abstract

A highly cross-linked porous polymer resin based on styrene–divinylbenzene matrix with pores created by the use of micellar imprinting technique was used as chromatographic packing material. Its performance as a column packing material in inverse size-exclusion chromatography was compared with a non-imprinted resin of the same polymer matrix. The porous structures (the pore size and the porosity) of the resins in the dry and wet states and their relationships with the elution volume of probe solutes (alkanes and polystyrene standards) were established. Characteristic properties of the resins such as specific pore volume, specific surface area and porosity are compared with results obtained by other methods of characterization such as mercury intrusion porosimetry, solvent regain and nitrogen sorption. The results show that the new porous resin can be used in the separation of small molecules. The separation is based on the size of the molecules, and the larger pores (meso- and macropores) in the porous resin can provide a much easier access to the smaller pores (micropores) which are useful in the chromatographic separations.

Keywords: Stationary phase; SEC; Styrene–divinylbenzene

1. Introduction

Porous structure is one of the most important features of a chromatographic packing material. Several analytical methods can be used to investigate the characteristics of pores, including mercury intrusion porosimetry [1–3], sorption or desorption of an inert gas (BET) [4,5], small angle X-ray scattering [6], differential scanning calorimetry [7] and, more recently, fluorine NMR spectroscopy [8].

Size exclusion chromatography (SEC) can be used to measure precisely the size of an unknown solute. When the solute size is known, SEC measurements can be used to characterize the porous structure of the packing material. The method is thus called inverse size-exclusion chromatography (ISEC). This technique was first developed by Aggerbrandt and Samuelson [9] who used poly(ethylene glycol) to determine the pore size distribution in cellulose fibers. Many studies helped to establish the theoretical and methodological basis of the technique [10–22]. The fundamental aspect of both theory and practice of ISEC was reviewed extensively by Gorbunov et al. [23] who summarized the mathematical models used in the evaluation of the experimental

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data. The conditions required for the correct realization of the method were also discussed. In the 1990s many researchers made use of the so-called chromatographic porosimetry in the study of gels [24–28]. Hagel et al. [29] reviewed the method in 1996. ISEC has been used in the study of the morphological supramolecular structure of swollen gels. It is particularly useful for the porosimetry of sorbents used in chromatography of polymers since the pore size distribution determined with SEC corresponds to the chromatographic distribution of the macromolecules. It is assumed that the distribution of flexible chains between a solvent and a porous medium is determined by their hydrodynamic radius R_h and pore size [30].

We have made new porous polymer resins based on styrene (S) and divinylbenzene (DVB) matrix [31,32]. The pores in the polymer resins were created by the reverse micelles of sodium bis(2-ethylhexyl)sulfosuccinate (AOT) dissolved in the mixture of comonomers prior to the initiation of the polymerization. The size of the pores was adjusted by the amount of water contained in the reverse micelles. The characteristics of the resins have been determined in the dry state by BET sorption and desorption with nitrogen. In this study, the characteristics (specific surface area, pore volume, pore radius and pore size distribution, and porosity) of selected polymer resins in the wet state are studied and the use of such resins as chromatographic column packing material is evaluated.

2. Experimental section

The polymer resins used were prepared by bulk polymerization as described previously [31]. The factors affecting the porosity of the resin have been studied [32]. AOT was dissolved in the mixture of the comonomers at a concentration of 0.2 *M*. The water-to-AOT molar ratio (W) in the reverse micelles was fixed at 12. The amount of the crosslinker (DVB) used was set at 50 vol%, but the purity of DVB was 55%, which means that the actual degree of crosslinking is ca. 27.5%. Bulk polymerization was initiated upon the addition of 2 wt% of AIBN followed with ultraviolet (UV) irradiation at wavelength of 254 nm. The resulting resin (RW12) was then ground and washed in a Soxhlet extractor. It was then dried, sieved and the fraction with particle size <120 mesh (less than 125 μm in diameter) was used in the ISEC study. The non-imprinted resin (RW0) was synthesized under the same conditions with the same degree of crosslinking but without the AOT reverse micelles. A density of 1.1 g/ml was used in the calculation for both polymer resins.

ISEC was used to characterize the porous structure of both resins (RW12 and RW0) in the swollen state. The columns (25×0.4 cm ID) were packed with the sorbents under pressure by the floating procedure in order to prepare good columns with a homogeneous resin-bed. The packing equipment consisted of a micropump LC 3001 (Laboratorni Pristoje, Praha), a filling column with an internal diameter of 1 cm and fitted with a manometer, which helped to monitor the pressure. The sorbent was suspended in tetrahydrofuran (THF) and poured in the filling column. It was then pumped through the analytical column, the outlet of which was fitted with a stainless steel fritted disc retained by a large-bore compression fitting until the increasing pressure stabilized at a constant value. The procedure took about 2 h.

Alkanes (C5–C32) and polystyrene standards (molecular weights ranged from 500 to 3.3×10^6) (Polymer Laboratories) were chosen as probes (Table 1). They are known to be non-adsorbent on this kind of materials [11,20]. The molecular mass distribution M_w/M_n for the PS standards ranges from 1.02 to 1.08 except for the PS sample with lowest $M_{w,}$ which displays a polydispersity index of 1.15. For all the probes, the detection was made with a refractive index detector on the ISEC system. The exact hydrodynamic dimensions L for the PS were calculated from the molecular mass M_r by the use the following equation [33]:

$$L\ (\text{nm}) = 0.0246\, M_r^{0.588} \quad (1)$$

The probe molecules (20 μl, 1 wt% THF solution) were injected and separated individually at a flow-rate of 1 ml/min with freshly distilled THF as eluent.

The specific surface area (S_g, m^2/g) in the dry state was determined by the three-point BET method using a Quantachrom apparatus (Model OS-67,

Table 1
The probe molecules and their retention volumes in the inverse size-exclusion chromatography with the polymer resins[a]

Probe molecule		M_w	L (nm)	M_w/M_n	V_e (ml)	
					RW0	RW12
Alkanes	C5	72.1	0.55		2.38	2.31
	C6	86.2	0.59		2.29	2.30
	C7	100.2	0.63		2.26	2.23
	C8	114.2	0.67		2.14	2.20
	C9	128.3	0.70		2.14	2.18
	C10	142.3	0.74		2.09	2.17
	C12	170.3	0.82		2.08	2.17
	C18	254.5	1.04		2.01	2.06
	C24	338.7	1.27		1.96	2.09
	C32	450.8	1.57		1.96	2.07
PS standards	1	580	1.9	1.15	1.89	2.04
	2	1300	3.8	1.08	1.87	2.04
	3	4950	13.6	1.03	1.92	1.91
	4	9860	26.7	1.02	1.92	1.91
	5	28 500	76.5	1.03	1.91	1.91
	6	72 200	193	1.02	1.89	1.91
	7	151 700	405	1.02	1.86	1.90
	8	426 600	1139	1.03	1.88	1.87
	9	1 290 000	3445	1.05	1.87	1.83
	10	3 390 000	9052	1.06	1.85	1.81

[a] Conditions: Resin samples RW0 and RW12, particles <120 mesh size. Columns: 25×0.4 cm I.D. Flow rate:: 1 ml/min. Samples injected: 20 μl of 1 wt% solution in THF.

Quantachrom Corp.) with dynamic nitrogen desorption method. The pore volume (V_g, ml/g) was assessed by the cyclohexane regain method. In this technique, the resin was first swollen in cyclohexane and the gel slurry so obtained was centrifuged to remove the extra-particle liquid. The solvent regain was then determined gravimetrically [11]. Mercury porosimetry was used to characterize the resins with a Carlo Erba Series 2000 apparatus in the pore size range 3.7–2500 nm.

3. Results and discussion

The probe concentration is chosen to facilitate the accurate identification of the chromatogram peak. The injected volume of the probe solutions was fixed low (20 μl) to prevent an overloading of the column which could decrease the overall quality of the recorded chromatogram. The imprinted resin (RW12) was used in comparison with the non-imprinted one (RW0). Under the same testing conditions, the overall peak quality was better for the whole series of injected alkanes when RW12 was used. The result is illustrated for two alkanes (pentane and octane) where very symmetrical traces are obtained with RW12 (Fig. 1A) while distorted chromatograms are recorded in the case of RW0 (Fig. 1B). The same observation also holds for the polystyrene standards series (Fig. 2). This indicates an overloading of the column packed with the RW0 resin despite its high micropore content (Table 2). The elution volumes recorded are given in Table 1. They were used to determine the upper and the lower exclusion limits of the porous packings as well as the distribution coefficients and the accessible porosity. The two samples (RW12 and RW0) display different porosimetric patterns as shown in Table 2, as well as in Fig. 3. The results in Table 2 indicate that the pore size distribution of RW12 packing comprises three groups of pores: micropores (<2 nm), mesopores (2–50 nm) and macropores (>50 nm). Fig. 3A shows the distribution of the pore sizes for RW12 and its cumulative pore volume. More illustrative is

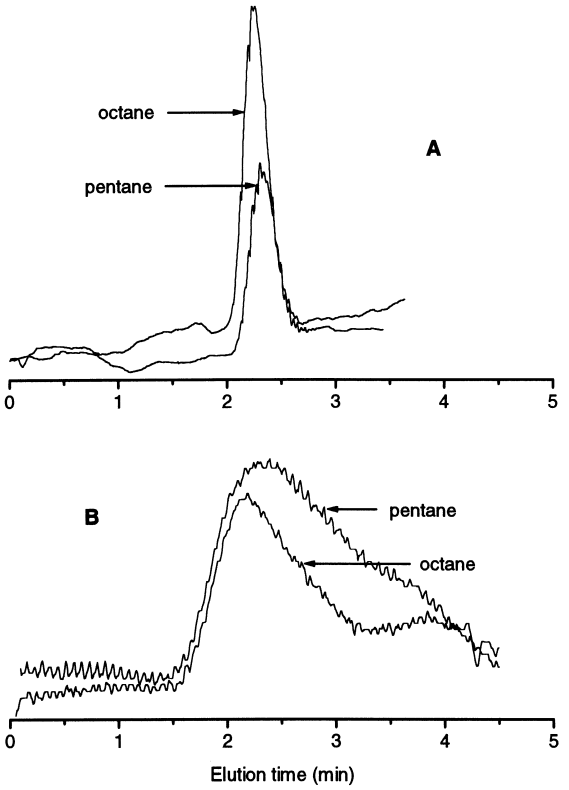

Fig. 1. Characteristic chromatograms of pentane and octane probes (20 μl of 1 wt% alkane solution in freshly distilled THF) obtained by eluting at 1 ml/min. Packing materials: (A): RW12 (S:DVB=1:1, AIBN=0.2 *M*, [AOT]=0.2 *M*, [Water]/[AOT]=12, particle size <120 mesh); (B) RW0 (S:DVB=1:1, AIBN=0.2 *M*, particle size <120 mesh). The column size was 25×0.4 cm I.D.

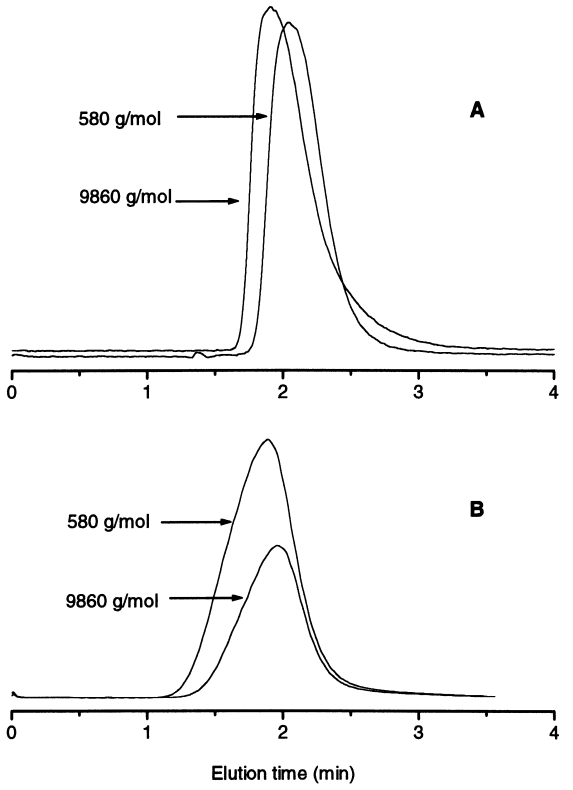

Fig. 2. Characteristic chromatograms of two polystyrene standards obtained by injecting 20 μl of 1 wt% polymer solution in freshly distilled THF. Packing materials: (A) RW12; (B) RW0. The characteristics of the resins and the columns are the same as in Fig. 1.

the distribution curve, which shows a peak in the microporous region at 0.6–1.5 nm. It indicates also the presence of meso- and macropores, the size of which is centered at ca. 10 nm. The sample RW0 contains mainly micropores in the size range of 0.6–1 nm, along with very small proportions of the meso- and macropores. It appears that the overall pore volume for each resin amounts to approximately 0.6 ml/g. It is predominantly due to micropores. However, the amount of micropores (0.307 ml/g) in sample RW12 is half of that in sample RW0 (0.541 ml/g). It is likely that the smaller pores in RW12 may be merged by the presence of the larger pores. Although meso- and macropores are not needed in the separation process, they are important to the transport of the molecules to the separation centers (micropores). The absence of this category of pores in the non-imprinted resin (RW0) makes the access to the micropores difficult and hence decreases its loading capacity. The micropores helps in the separation of small molecules up to the molecular mass

Table 2
Pore size distributions for RW0 and RW12 as determined by ISEC

Type of pores	Pore diameter (nm)	Pore volume (ml/g)[a]	
		RW0	RW12
Micropores	<2	0.541	0.307
Mesopores	2–50	0.033	0.154
Macropores	>50	0.011	0.103
Total		0.585	0.564

[a] Calculated for polymer density 1.1 g/ml.

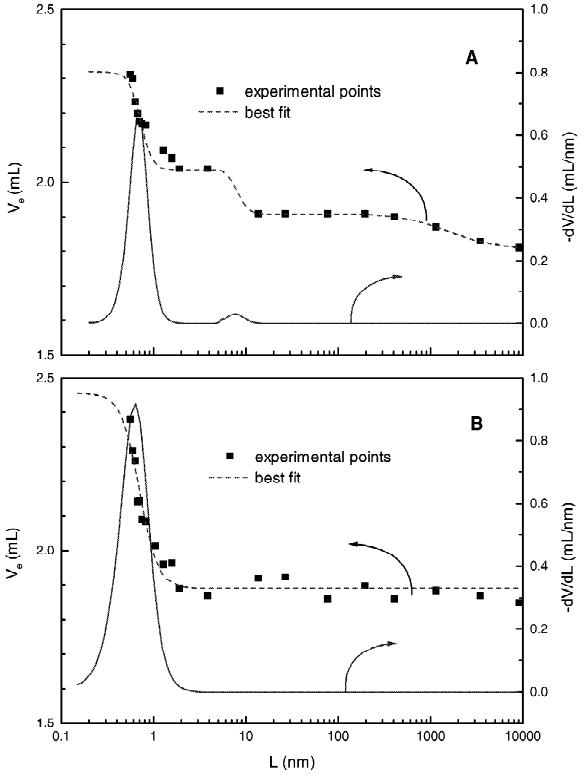

Fig. 3. The distribution curve of the pore sizes and the cumulative pore volume as obtained from ISEC. The distribution curve is shown as the derivative of the mathematical fit of the cumulative curve of the pore sizes: (A) RW12; (B) RW0.

of 580. All the molecules with molar mass greater than 580 are excluded (Fig. 2) and therefore cannot be separated by the size-exclusion mechanism.

The distribution coefficient is calculated for species i according to:

$$K_{Di} = \frac{V_i - V_0}{V_1 - V_0} \quad (2)$$

where V_i is the elution volume of the species i, V_0 and V_1 those of the largest and smallest probes (polystyrene with molar mass of 3 390 000 and pentane, respectively) (Table 1). If the logarithm of the distribution coefficient K_D is plotted as a function of the probe size L, linear relationships are obtained with a correlation coefficient of 0.993 and 0.951 for RW12 and RW0, respectively (Fig. 4). This confirms the presence of micropores shown on the pore size distribution curves in Fig. 3.

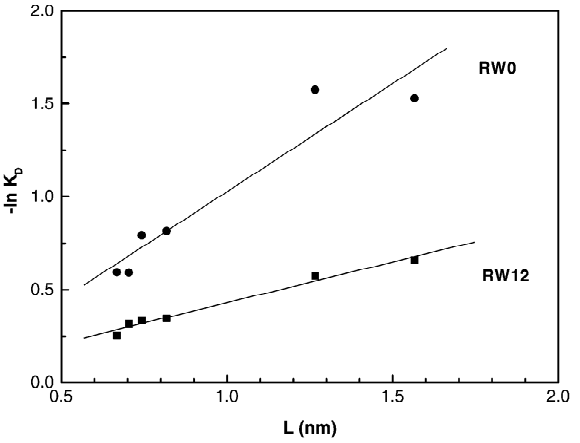

Fig. 4. Distribution coefficient K_D of the alkane probes versus the characteristic dimension L given for RW12 (■) and RW0 resins (●).

The results from mercury porosimetry, normally used to determine the meso- and macropore contents, supported globally those from ISEC (Fig. 5). A low content of macropores was observed. But it is not possible to measure pores smaller than 3.7 nm in size. Therefore the micropore area which is important for the separation cannot be determined precisely by this technique. The overall contents of pores for RW12 and RW0 are 0.594 and 0.402 ml/g, respectively, as measured by mercury porosimetry (Table 3).

Table 3 compares the overall characteristics (pore volume V_g, specific surface area S_g, and porosity p) of the two resins as obtained by different methods. The specific pore volume, V_g, from ISEC can be calculated from $V_g = (V_1 - V_0)/G$, where V_1 and V_0 are as defined above and G is the weight of the sample in the column.

The V_g values from the other methods are derived directly without further calculation. It is known that the porosimetric patterns obtained by these various techniques usually differ [34]. For RW12 resin, the value obtained with mercury porosimetry where mercury is forced through the porous structure of the matrix is slightly higher than that given by ISEC (0.594 and 0.564 ml/g, respectively) (Table 3). This means that this resin has the same porosity in the dry and the swollen state. It is termed permanent porosity. However, the RW0 resin has a higher pore

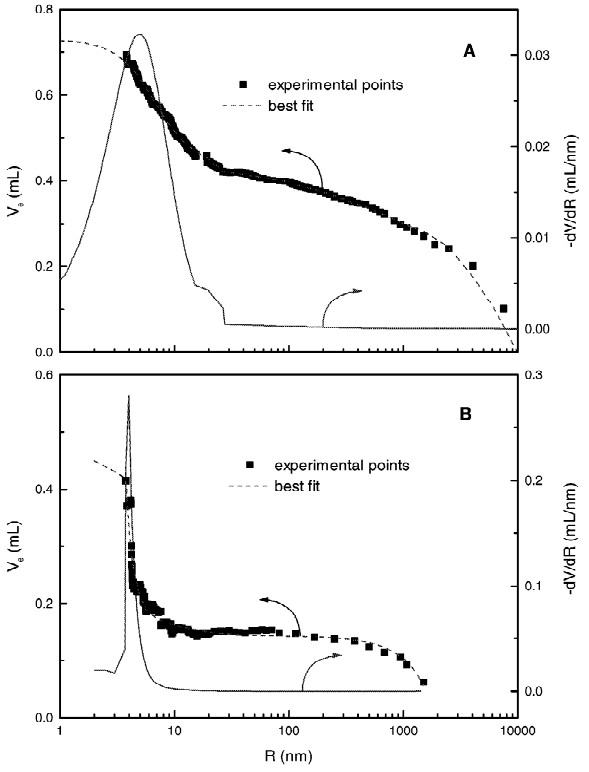

Fig. 5. The distribution curve of the pore sizes and the cumulative pore volume as obtained from mercury porosimetry: (A) RW12; (B) RW0. The distribution curves are obtained in the same way as in Fig. 3.

volume in the swollen state (0.585 ml/g) than in the dry state (0.402 ml/g) (Table 3). This means that the non-imprinted resin RW0 undergoes a more extensive swelling, but it does not retain porosity in the dry state. This is supported by the low specific surface area (0.35 m^2/g) obtained by BET (Table 3). It is possible that the presence of larger pores in the imprinted resins (RW12) reduces the relative swellability of the resin at a given degree of crosslinking, when compared with the non-imprinted one (RW0). Both samples (RW12 and RW0) display a swelling porosity that can be evidenced only by ISEC measurements.

Porosity is usually defined as the ratio between the pore volume and the total polymer volume:

$$p = \frac{V_g}{V_g + \frac{1}{d}} \times 100\% \quad (3)$$

where V_g is the specific pore volume (ml/g) and d is the polymer density (for S-DVB copolymer, $d = 1.1$ g/ml). In both cases (RW12 and RW0), the conclusions drawn for porosity (Table 3) should be similar to those drawn for porous volume as stated above.

Compared with polymers prepared by suspension polymerization technique, the total pore volumes of these resins are much smaller. In comparison, with non-polar copolymers in which polar co-monomers are involved, the amount of micropores decreases while the amount of macropores increases [35], since the pores are formed through a phase separation mechanism in the organic phase. The pore volume of the resins prepared by suspension polymerization is determined by the amount of the inert solvent used for diluting the starting monomers.

4. Conclusion

The polymer resins possess some characteristic properties of copolymers prepared by bulk copolymerization: low pore volume and also, in the case of non-polar monomers, prevailing amounts of micropores. In fact, the pore volume of imprinted sample RW12 still consists mainly of micropores. The high

Table 3
Comparison of the pore volume (V_g), specific surface area (S_g) and porosity (p) determined by different methods

Method	V_g (ml/g)		S_g (m^2/g)		p (%)[a]	
	RW0	RW12	RW0	RW12	RW0	RW12
Solvent regain	0.285	0.457	–	–	23.9	33.5
Hg-porosimetry	0.402	0.594	–	77	30.7	39.5
BET	–	–	0.35	9	–	–
ISEC	0.585[a]	0.564[a]	–	–	38.2	38.3

[a] Calculated for polymer density 1.1 g/ml.

content of micropores is useful in the separation of small molecules such as alkanes used in this study, while the larger pores helps in the transport of the molecules during the separation. The presence of mesopores and macropores in the matrix of the imprinted polymer sample RW12 improves the accessibility to the microporous cavities. In comparison, the non-imprinted sample RW0 contains only micropores, which may not be accessible by the alkanes.

It is shown that the specific surface area and/or pore volume measured in the dry state do not necessarily reflect the situation during the applications due to the swellability of the gel. In a good solvent, the polymeric structure may still manifest swellability even with 27.5 vol% of pure crosslinker DVB copolymerized in the absence of an inert solvent. It is worth mentioning that a disadvantage of the bulk copolymerization is the difficulty to prepare regular spherical beads. Therefore, the use of suspension or emulsion systems (for example, a water-in-oil-in-water system) should provide such porous materials in spherical forms that would be more suitable for chromatographic applications. Alternatively, the use of monolithic crosslinked polymers as packing materials has been shown to be promising [36–38]. It can be also tested for these reverse micelle-imprinted polymers.

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