

The Determination of the Pore Structural Parameters of Isoporous Resins by Inverse GPC*

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SYNOPSIS

The swollen pore structure of a series of microporous isoporous resins (7.4–140 Å) are investigated with inverse GPC, *n*-alkylbenzenes and linear polystyrenes being used as probe molecules. The results indicated that, with the lowering of crosslinking degree of isoporous resins, the average pore diameter increased and the pore distribution curve broadened. All pore volume distribution obeyed a log-normal distribution. Based on the linear regression method, the experimental data were fitted to a monotonously declining exponential function and a normal distribution function by a computer, and some important structural parameters such as average pore diameter, pore volume distribution, specific surface area, etc. were obtained. The specific surface area of swollen gels were found much greater than those in the dry state measured by N₂ adsorption.

INTRODUCTION

Porous polymer materials are widely used as ion exchange resins, adsorbents, and carriers for catalysts; they are usually used in the swollen state, which makes their porous structure highly dependent on the medium employed. The classical methods for determining porous structure such as nitrogen adsorption and mercury porosimetry are only good for dry samples and cannot be used to provide information on pore structure in the moistened or swollen state.

Gel permeation chromatography (GPC) is a widely employed method for separation of dissolved substances—mostly polymer mixtures—according to their molecular size. Conversely, by means of the retention data of probes of known molecular size, pore volume distribution and other pore structural parameters can be determined when porous materials are used as the stationary phase. This method was first proposed by Halasz et al.^{1–3}; Freeman and others explained the distribution mechanism of inverse GPC (IGPC) via the theory of Giddings,⁴ and

further stated the nonenthalpic conditions for measurements with IGPC.^{5,6} The relationship between distribution coefficient *K* and elution volume *V_e* can be written as

$$V_e = K \cdot V_p + V_0 \quad (1)$$

where *V_p* is the pore volume of the porous system and *V₀* is the interstitial volume of the column.

Although several investigations on the determination of macroporous organic gels by IGPC have been reported,^{6–9} reports on the determination of microporous system in the swollen state are rare.^{5,10} The purpose of the present work is to characterize the pore structure of a new type of crosslinked copolymer, isoporous resin, inspect the homogeneity of its structure, and study the effect of crosslinking degree on the pore structure. We hope to establish a quantitative relationship between the distribution coefficient *K* and the dimensions of probe molecules through fitting with the chromatographic data using a computer and find from this the pore structural parameters of isoporous resins.

Crosslinked styrene-divinylbenzene copolymer is a widely used polymeric carrier, but the distribution of crosslinking bridges in it is not uniform. In comparison with this, isoporous gels having a statistical distribution of crosslinking bridges, can be obtained by crosslinking of polystyrene chains with bifunc-

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tional compounds in solution or in the swollen state. The term *isoporous* is used here to differentiate it from the inhomogeneous products of ordinary copolymerization, in comparison with which the isoporous resins are characterized by considerable elasticity (change in volume), greater swelling capacity in poor solvents, greater porosity and specific surface area, etc.

There have appeared in recent years criticisms of Halasz's work for the determination of porous structure from IGPC data.^{11,12} We applied Halasz's method, with some modifications in data treatment, to microporous isoporous resins and obtained some meaningful results. We present our work in this paper in the hope of arousing interest and criticisms on it.

EXPERIMENTAL

Two steps were involved in the preparation of isoporous resins used as the chromatographic stationary phase:

1. Synthesis by the general procedure of the lightly crosslinked ST-DVB (2%) particles ($< 50 \mu\text{m}$) by stirring under high speed.
2. A solution of 3.84 g (0.0173 mol) of *p*-xylenedichloride in 70 mL dichloroethane was added to 6 g (0.0577 mol) of copolymer of ST-DVB (2%) and the mixture was held at room temperature for 24 h for swelling of the particles. After 5.42 g (0.021 mol) of SnCl_4 in 10 mL of dichloroethane was added, the mixture was carefully stirred and heated at 70°C for 8 h. The isoporous resin of 43% crosslinking degree formed was washed successively by acetone, deionized water, and 10% HCl, three times each, and fractionated by sedimenta-

tion. The fraction of particle size $15\text{--}30 \mu\text{m}$ was collected and extracted in a Soxhlet extractor.¹³ See Ref. 14 for detailed synthesis and fractionation procedures. The crosslinking degree of isoporous resins was calculated from the composition of the initial reaction mixture (i.e., the bridge fraction of the total number of the network structural elements—unsubstituted phenyl rings and crosslinking bridges).

A definite amount of the resin was swollen in a small amount of THF to form a paste which was pressed into the chromatographic column ($5.0 \times 250 \text{ mm}$) by a large quantity of solvent under high flow rate ($10\text{--}20 \text{ mL/min}$). The column was rinsed at a flow rate of 1 mL/min for 10 h, so as to make the column bed absolutely stable. The number of theoretical plates toward benzene of the chromatographic column filled in this way could reach a value of $1000\text{--}5000 \text{ m}$, which is sufficient for the symmetry of chromatographic peak if the individual probes are injected independently.

THF (AR) was used as the eluent. Its solubility parameter is nearly equal to that of ST-DVB copolymer (the chemical structure of isoporous resin can be taken to be that of highly crosslinked ST-DVB copolymer) and therefore can fulfill the non-enthalpic condition of GPC determinations. The anhydrous THF was distilled in the presence of cuprous chloride and used as soon as possible after degasification with ultrasonic wave.

The values used to characterize the pore dimensions of the stationary phase were determined from the effective dimensions of the probe molecules shown in Table I. The L values of polystyrene standards were calculated according to Halasz. It is the diameter of the smallest pores in the swollen solid

Table I L -Values^a of Probe Molecules

Standards	Grade	L (Å)	Standards	Mol Wt	M_w/M_n ^b	L (Å)
Benzene	AR	7.4	PS-1	526	1.1	25
Ethylbenzene	CP	8.5	PS-2	800	1.1	31.6
			PS-3	2550	1.08	61.7
<i>n</i> -Butylbenzene	CP	10.5	PS-4	5700	1.06	93.9
			PS-5	10,010	1.09	140.3
<i>n</i> -Hexylbenzene	^c	13.4	PS-6	26,700	1.05	248.4
<i>n</i> -Octylbenzene	^c	15.9	PS-7	52,600	1.08	370.1
			PS-8	397,000	1.36	1214.7
<i>n</i> -Dodecylbenzene	^d	20.8	PS-9	560,000	1.09	1850.0

^a Exclusion value of the diameter of the smallest pores permeable to the probe molecules; see Ref. 2.

^b Data provided by the producers.

^c Synthesized and purified in our own laboratory and proved by MS, $^{13}\text{C-NMR}$, and GC to be of high purity.

^d Purified by the preparative chromatography and proved by GC to be satisfactory chromatographically.

penetrable to pst standard of weight average molecular weight M_w from the formula

$$L (\text{\AA}) = 0.62 M_w^{0.588}$$

This is interpreted as the minimum effective pore diameter which exerts no steric hindrance to penetration of the corresponding pst molecules.

The chromatographic apparatus consisted of a micropump of constant flow, a sampling valve, a volumetric flowmeter, a chromatographic micro-computer, and an ultraviolet detector (Shanghai Analytical Instruments, China). The elution volume is taken to be the product of the period of time from the injection of the probe to the appearance of the vertex of the symmetric peak and the flow rate of the eluent. The flow rate was regulated at 1 mL/min. The concentration of the probe was around 0.1% (w/v). The observation for each probe was repeated at least three times and the average was taken. The duplicability of the elution volume was better than 1%. The isoporous resins inside the column was extruded, dried, and weighed after the measurement. The volume of the empty column, V_c ,

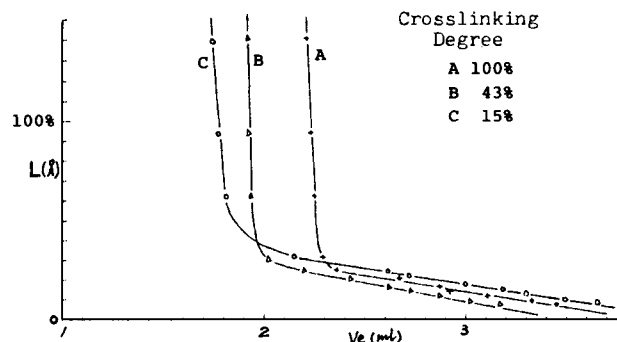


Figure 1 Elution curves of isoporous resins of three degrees of crosslinking.

was found from the difference in weight of the column after filling with water and emptying.

RESULTS AND DISCUSSION

The isoporous resins are the product of two cross-linking reactions, the second one with *p*-xylene dichloride being more important. The density of

Table II Experimental Data of Isoporous Resin (43% Crosslinking Degree)

Probes	$L (\text{\AA})$	$\log L$	$T (\text{min})$	K	$\Delta K / \Delta \log L$	$\log \bar{L}$	$\bar{L} (\text{\AA})$
1	7.4	0.8692	3.3033	1			
2	8.5	0.9294	3.1433	0.8829	1.9452	0.8993	7.9305
3	10.9	1.0374	2.9867	0.7683	1.0611	0.9834	9.625
4	13.4	1.1271	2.8467	0.6659	1.1416	1.0623	12.0865
5	15.9	1.2014	2.7267	0.5781	1.1817	1.1643	14.5982
6	20.8	1.3181	2.5367	0.4390	1.1919	1.2598	18.1886
7	25	1.3979	2.2933	0.2609	2.2318	1.358	22.8034
8	31.6	1.4997	2.11	0.1268	1.3173	1.4488	29.1061
9	61.7	1.7903	2.0233	0.0634	0.2182	1.645	44.157
10	93.9	1.9727	2.0067	0.0512	0.0669	1.8815	76.120
11	140.3	2.1471	1.9933	0.0414	0.0562	2.0599	114.789
12	248.4	2.3952	1.98	0.0317	0.0391	2.2712	186.724
13	370.1	2.5683	1.9733	0.0268	0.0283	2.4818	303.249
14	1214.7	3.0845	1.95	9.7E-03	0.0331	2.8264	670.502
15	1850	3.2672	1.9367	0	0.0531	3.1759	1499.34

Table III Results of Determination of Isoporous Resins

Crosslinking Degree of Sample (%)	N ₂ Adsorption			Inverse GPC			Normal Distribution			Pore Volume Distribution			
	Specific Surface Area (m ² /g)	Specific Pore Volume (ml/g)	Swelling Ratio	Specific Surface Area (m ² /g)	Specific Pore Volume (ml/g)	Porosity	Av. Pore Diam. (Å)	Square Deviation	Correlation Coefficient	Most Prob Pore Diam. (Å)	Av Pore Diam. (Å)	L ₉₀ (Å)	Correlation Coefficient
100	33.60	0.4602	1.36	1702	0.6732	0.4487	14.9	0.1915	0.982	12.6	14.9	15.1	0.982
82			1.49	1643	0.7362	0.4646	15.4	0.1916	0.984	13.4	15.4	15.4	0.982
67	25.26	0.3575	1.57	1662	0.8264	0.4925	16.3	0.2041	0.981	13.9	16.4	16.2	0.985
43			1.68	1975	0.8633	0.4987	16.6	0.2460	0.993	12.7	16.7	16.9	0.994
25			1.94	1979	0.9534	0.5020	18.6	0.3135	0.986	12.6	18.9	18.7	0.992
15			2.15	2226	1.249	0.5931	21.8	0.330	0.990	13.9	21.9	21.8	0.993

crosslinking bridges determines the pore volume distribution or average pore diameter becoming narrower and smaller as the degree of crosslinking increases. The degree of crosslinking of isoporous resins is usually calculated from the composition of the reaction mixture where the Friedel-Crafts reaction takes place.¹⁵ One of authors has tried to find the secondary degree of crosslinking by means of pyrolysis chromatography.¹⁶ As an actual example, the experimental data for isoporous resins of 43% secondary crosslinking is listed in Table II.

According to eq. (1), if the probe molecule is so large as to be excluded by all pores, then $V_e = V_0$ and $k = 0$, but if it is small enough to diffuse into all pores, then $V_e = V_p + V_0$ and $k = 1$. If the mass of the pore material is M , then the specific pore volume $V_{p,s}$ is

$$V_{p,s} = \frac{V_p}{M} = \frac{[(V_p + V_0) - V_0]}{M} \quad (2)$$

and porosity P , the fraction of the volume of porous substances occupied by pores, is

$$P = V_p / (V_p + M / \rho_m) = V_p / (V_c - V_0) \quad (3)$$

where ρ_m is the skeletal density in the swollen state and V_e is the sum of volumes of empty column and connecting tubes.

From the elution curves in Figure 1, we have selected the elution volume of ps-4 probe ($M = 5100$), the interstitial volume V_0 . In order to avoid the use of old methods of calculation for the microporous system of isoporous resins for integral and differential distribution curves, we decided to fit the experimental data directly with a function. Warren et al.¹⁷ fit the data for many chromatographic column supports by polynomials of first to sixth orders and found that a fifth order polynomial gives the best fit. But in the whole value range of K (0-1), extreme values, inflection points, or even negative values may appear and, furthermore, for supports of narrow pore size distribution, fitting with a polynomial rarely gives better effect. In this paper, we use a monotonously declining exponential function of the form¹⁸

$$K = 1 / (1 + aL^b) \quad (4)$$

to fit the experimental data, where a and b are of undetermined values. After rearrangement and taking logarithms of eq. (4), a linear regression equation (5) can be obtained. Taking the K value of each probe in the form of $\log[1/(K - 1)]$ except those at both ends

$$b \log L + \log a = \log[1/(K - 1)] \quad (5)$$

where the value of K is 0 or 1, and plotting against the corresponding value of $\log L$, a straight line should be obtained. In the case of good correlation coefficient, we can find values of a and b from the slope and intercept of the linear plot. All samples show good linear relationships with correlation coefficients listed in Table III. The regression equation for the sample of 43% crosslinking is shown in Figure 2. Curve A in Figure 3 shows the theoretical integral distribution (K - L curve) fitted by the exponential function. The results of both correlation coefficient and visual inspection are satisfactory. The values of L corresponding to 50% of pore volume (L_{50}) and correlation coefficients of all samples are given in Table III. By taking the absolute value of dK/dL from eq. (4), we obtained the theoretical differential distribution curve given by

$$|dK/dL| = abL^{b-1}/(1 + aL^b)^2 \quad (6)$$

(see curve B in Fig. 3). In order to show this curve more clearly, the value of $|dK/dL|$ was increased tenfold. The value of L on the abscissa which corresponds to the maximum value of the differential distribution curve is taken as the most probable pore diameter. By transformation of coordinates we have

$$|dK/d \log L| = 2.303abL^b/(1 + aL^b) \quad (7)$$

Plotting it against L , curve C in Figure 3 is obtained, and the abscissa corresponding to the maximum of this curve is the average pore diameter. If the $|dK/d \log L|$ is plotted against $\log L$ instead of L , an entirely symmetrical distribution curve will result (curve B in Fig. 4). Table III gives the fitting results of all samples. These fitting curves show that, in most districts, the theoretical fitting curve can fit the experimental points pretty well, both in the po-

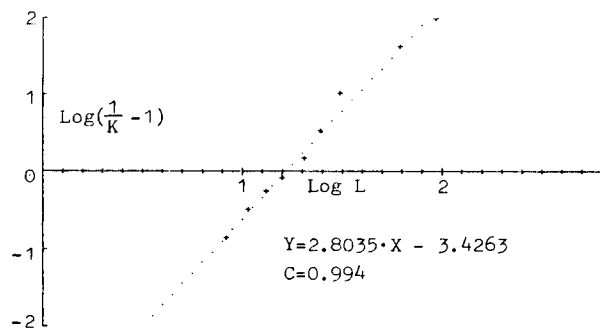


Figure 2 The linear regression equation of the sample of 43% crosslinking degree.

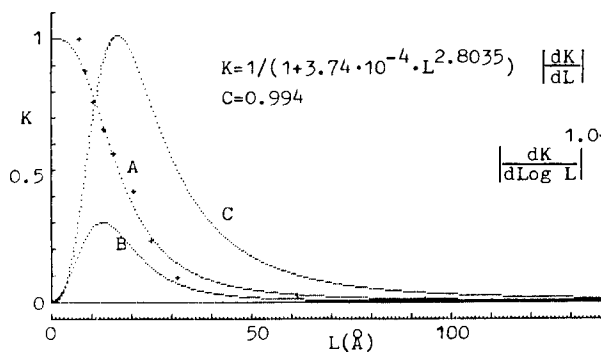


Figure 3 Theoretical fitting curves of the sample of 43% crosslinking degree: (A) K - L curve; (B) $10 \cdot |dK/dL|$ - L curve; (C) $|dK/d \log L|$ - L curve.

sition of the curve and its gradient, but at both ends of the curve, the fitting is poorer. This deviation is to be expected, because even such small molecules like benzene or the eluent still possess definite molecular dimensions and cannot diffuse completely into all pores. Therefore, the smallest probe molecule should have a K value close to 1 but not equal to 1. The largest ones are also not completely excluded by the pore system, resulting in a K value close to 0 but not equal to 0. The theoretical fitting curves emphasize that even for entirely homogeneous pore systems, there is no sudden change from total diffusion to total exclusion.

We plot also K_i vs $\log L_i$ with normal probability coordinate on a normal probability paper in the hope of obtaining a linear relationship with good correlation coefficient, showing that the pore system obeys a log-normal distribution. The fitting is done on a computer. The expectation value μ (the $\log L$ value on this straight line corresponding to $K = 50\%$) and the square deviation σ of this normal distribution (the absolute difference in $\log L$ coordinate corresponding to $K = 50\%$ and $K = 15.9\%$ or

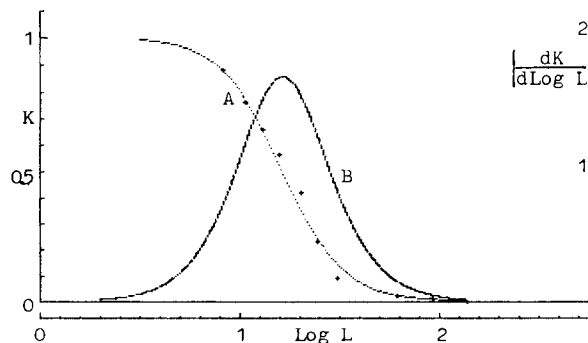


Figure 4 Theoretical fitting curves of the sample of 43% crosslinking degree: (A) K - $\log L$ curve; (B) $dK/d \log L$ - $\log L$ curve.

$K = 84.1\%$) were determined from the intercept and slope of the straight line. These curves for four samples of isoporous resins were shown in Figure 5, their μ and σ values being given in Table III.

From Figure 5 it is evident that with the lowering of degree of crosslinking the average pore diameter gradually increases and the distribution curve broadens; this tendency is quite evident, although the change is quite moderate. Taking the pores as continuous cylinders opening at both ends, the specific surface A is given by

$$A \text{ (m}^2/\text{g)} = 4 \times 10 V_{p,s} \text{ (cm}^3/\text{g)} L_m \text{ (\AA)} \quad (8)$$

where $V_{p,s}$ is the specific surface area and L_m is the average pore diameter. If the pores are not all open, the error in specific surface is less than 5% provided that the cylindrical pores are five times as long as their diameters. The results of surface shown in Table III are calculated according to eq. (8). For two samples of 67 and 100% crosslinking, we determined by N_2 adsorption their $V_{p,s}$ and A (using Sorptiomatic Series 1800 Carlo Erba) and the results are listed in Table III, showing a great difference from the values found above, which means that the pore structures of organic gels in the dry and swollen states are quite different. This is exactly the aspect that embodies the special features of measurement of pore structure for swollen state by IGPC.

All calculations, fittings, and plottings in this paper were executed on an Apple-II microcomputer by a BASIC program compiled by the authors. We have not tried on ordinary PS-DVB resins for comparison due to the comparative heterogeneity of the structure of these resins.

CONCLUSIONS

Using *n*-allylbenzene and linear polystyrenes as probes, we determined the pore structural param-

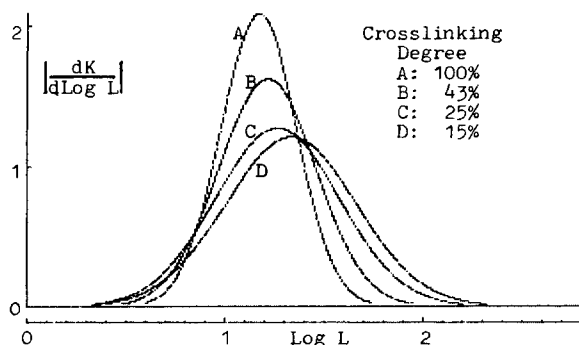


Figure 5 Theoretical fitting normal distribution curves of isoporous resins.

eters of a series of isoporous resins on the basis of principle of inverse GPC. The results of determination showed that, with the lowering of degree of crosslinking of the isoporous resins, the specific pore volume, porosity, and average pore diameter gradually increased, and the pore volume distribution gradually broadened with the use of a computer, experimental data were fitted with an exponential and normal function to obtain quantitative relationships between the distribution coefficient K and dimensions of probe molecules L , and further to derive several differential distribution curves and pore structural parameters. There is almost complete consistency of results obtained by these two types of fitting functions. The results of determination in dry and swollen state differ considerably, showing a change in structure under different conditions.

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