CHROM. 14,247

STUDIES OF CHROMATOGRAPHIC PACKINGS CONSISTING OF POROUS POLYMERS

II. SEPARATION PROPERTIES OF A POROUS STYRENE POLYMER CROSS-LINKED BY DI(METHACRYLOYLOXYMETHYL)NAPHTHALENES

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(Received July 30th, 1981)

SUMMARY

A cross-linked porous styrene polymer has been used for chromatographic separation of various classes of organic compounds and its properties have been compared with those of Chromosorb 101 and Porapak Q. This polymer shows higher initial decomposition temperatures than Chromosorb 101 and Porapak Q. Its usefulness as a column packing for gas chromatography has been estimated from polarities, numbers of theoretical plates, resolutions and retention times for various organic mixtures. Besides hydrocarbons, alcohols, carboxylic acids and ketones, the new column packing could be used for separation of amines.

INTRODUCTION

In practical gas chromatography (GC), the use of adsorption chromatography is increasing. This is connected with the development and application of a number of highly effective adsorbents with adequately homogeneous surfaces with respect to adsorption energy but different chemical properties. They are represented by graphitized carbon blac, zeolites, geometrically and chemically modified silica gels and porous glass[1].

Porous polymers are of special interest[2]. They are widely used in analytical and preparative GC owing to such features as their relatively high universality, the possitility of regulating their geometrical and chemical structure in the process of synthesis and sufficiently high thermal stability. Most of the porous polymers known to date were prepared from styrene and various cross-linking reagents, of which the most frequently used is divinylbenzene. In our laboratory, a mixture of di(methacryloyloxymethyl)naphthalenes consisting of the 1,4 and 1,5 isomers, m.p. 110–113°C, was used for the synthesis of porous polymers.

In this paper we present the results of studies of the chromatographic properties of the polymer (ST-DMN), formed from the above cross-linking agent and styrene, under optimal conditions as described previously[3]. The chromatographic

parameters obtained were compared with those of the known packings Chromosorb 101 (Johns-Manville) and Porapak Q (Waters Assoc.).

EXPERIMENTAL

Synthesis of the porous polymers

In a 50-l glass reactor supplied with a mixer, a back-cooler, a thermometer and a neutral gas (nitrogen) feed. 450 g polyvinyl alcohol were dissolved in 25.5 l distilled water and then heated to 70°C with constant mixing. After the polyalcohol had dissolved, 600 g of a mixture of the isomers 1,4- and 1,5-di(methacryloyloxymethyl)naphthalenes, 600 g styrene, 720 ml n-dodecane, 2400 ml toluene and 18 g of α,α'-azoisobutyronitrile as initiator were slowly poured into the reactor. The mixture was constantly stirred and heated at 70°C for 24 h. Suspension polymerization resulted in a copolymer in the form of beads, which. after separation from the post-reaction solution. were washed with distilled water (4 × 20 dm^3) at 85°C and 30-min intervals. Further washing of the copolymer was conducted at the boiling temperature of the solvent for about 1 h. The product was repeatedly extracted with acetone (11 × 7 dm^3). methanol (4 × 7 dm^3), benzene (3 × 7 l) and then again with methanol (2 × 7 dm^3). The purified porous copolymer beads were separated into fractions by the wet sieving. The following fractions were obtained: 0.2–0.15 mm, 26 wt. %; 0.15–0.1 mm, 35 wt. %; 0.1–0.088 mm. 14 wt. %; < 0.088 mm, 25 wt. %. These were first dried at 70°C for 2 h under reduced pressure. and then for another 2 h at 150°C under atmospheric pressure.

For chromatographic measurements. 0.15–0.2 mm grains were used the diameters of which approximated those of the graines of Porapak Q (80–100 mesh) and Chromosorb 101 (60–80 mesh).

Measurements of the specific surface area of polymers

These measurements were carried out by the method of thermal desorption of Nelsen and Eggertsen[4]. using an apparatus designed and constructed in the Department of Physical Chemistry. M. Curie-Sklodowska University[5]. Nitrogen was used as adsorbate and hydrogen as carrier gas. The specific surface area was calculated by the BET method. assuming that the area of a single nitrogen molecule is 16.2 Å^2. The measurements were preceded by activation of the samples at 200°C for 2 h in a hydrogen stream.

Thermogravimetric (TG) measurements

The measurements were carried out on a derivatograph (MOM, Budapest, Hungary). at a heating rate of 5°C/min in the range from 20 to 1000°C in the air. The initial decomposition temperature was determined from the course of the TG curve.

Chromatographic measurements

The chromatographic measurements were carried out on a Chromatron GCHF-18.3 gas chromatograph (Chromatron, Berlin. G.D.R.) equiped with thermal conductivity detector. Hydrogen at a flow-rate of 50 ml/min was used as carrier gas; the current of the bridge was 200 mA and the temperature of the injector was 250°C.

The studies were carried out on columns of stainless steel (100 cm $\times$ 4 mm I.D.). The measurements of retention indices for McReynolds substances were carried out at 140°C, whereas those of specific retention volume, V_m, were made at 180°C. The samples were injected by means of a 1-μl syringe (SGE, North Melbourne, Australia). For individual substances such as benzene, n-butanol, pentanone-2, 1-nitropropane and pyridine, trace amounts were injected, by dipping the syringe needle (at the zero position of the piston) in the sample colution for 1 sec[6]. Samples (0.2 μl) of the following mixtures were also injected: (1) aliphatic n-hydrocarbons (C_5–C_{12}); (2) ketones: dimethyl ketone, methyl ethyl ketone, methyl n-propyl ketone and methyl n-butyl ketone; (3) n-aliphatic primary alcohols (C_1–C_{10}); (4) n-aliphatic carboxylic acids: formic, acetic, propionic, butyric; (5) amines: ethylamine, diethylamine and triethylamine; (6) alcohol isomers: methanol, ethanol, propanol-1, propanol-2, butanol-2, 2-methylpropanol-1, butanol-1, pentanol-2, pentanol-3 and pentanol-1.

From the experimental data the number of theoretical plates, n, was calculated according to[7]

$$n = 5.54 \, (l_R/W_{n,2})^2$$

Where l_R = retention distance on the chromatogram and $W_{n,2}$ = peak width at half-height of the peak. The resolution, $R_{i,j}$, for a selected pair of compounds was calculated from[8]

$$R_{i,j} = 2\Delta t_R \, (w_{p,i} + w_{p,j})$$

where $\Delta t_R = t_{Ri,j} - t_{R,i}$, the distance between the maxima of the two peaks, and $w_{p,i}$ and $w_{p,j}$ are the widths of the peaks determined by extrapolating points of inlection of the peaks towards the baseline.

The retention index, I_x, of substance x was calculated from[9]

$$I_x = 100 \log (t'_{R,x}/t'_{R,z}) \, / \, (\log t'_{R,z+1} \, / \, t'_{R,z}) + 100 \, z$$

in which $t'_{R,x}$ denotes the reduced retention time of the substance, $t'_{R,z}$ the reduced retention time of the homologous alkane with the nearest shortest retention time, $t'_{R,z+1}$ the reduced retention time of the next higher homologue eluted after homologue z and z denotes the number of carbon atoms in the n-alkane molecule. The specific retention volume was calculated according to [10]

$$V_m = \frac{t_R \, W_{pom} P_{pom} \, T}{m \, T_{pom} P_o} \cdot f$$

where t_R denotes the corrected retention time, W_{pom} the volume velocity of carrier gas in the flow-meter, P_{pom}, T_{pom} the pressure and temperature in the flow-meter, T the temperature of the column and f the James–Martin coefficient.

DISCUSSION

Comparing the retention indices of McReynold substances given Table I, it can be seen that Porapak Q yields the lowest values, and ST-DMN the highest values, which accounts for the polar character of the latter. The high polarity of the ST-DMN packing is confirmed by the data given in Table II, which represent modified McReynolds constants relative those on graphitized carbon black[6,11,12]. The differences are connected with the presence of ester groups in the polymer skeleton.

TABLE I

KOVÁTS INDICES FOR McREYNOLDS SUBSTANCES ON THE STUDIED POLYMERS AT 140°C

Polymer	Benzene	Butanol-1	Pentanone-2	1-Nitropropane	Pyridine
Porapak Q	617	607	651	654	660
Chromosorb 101	706	708	747	797	835
ST-DMN	760	782	793	887	886

TABLE II
PROPERTIES OF THE POROUS POLYMERS

S = Specific surface area; t = initial decomposition temperature; n = number of theoretical plates for butanol-1; $R_{i,j}$ = resolution for the pair butanol-2–2-methylpropanol; x, y, z = modified McReynolds constants for benzene, butanol-1 and pentanone-2; I = total selectivity relative to graphitized carbon black. Measurement temperatures: n, $R_{i,j}$, 150°C; x, y, z, 140°C.

Polymer	S $(m^2 g)$	t	n	$R_{i,j}$	x	y	z	I
Porapak Q	660	200	790	0.48	43	118	86	247
Chromosorb 101	26	220	1053	0.83	132	219	182	533
ST-DMN	90	280	1086	1.08	186	293	228	707

From the data given in Table II it appears that the ST-DMN packing occupies an intermediate position as regards the specific surface area, but is characterized by the highest decomposition temperature as estimated from the TG curve. This feature permits application of the polymer to chromatographic separations at higher working temperatures. This is of particular value in the analysis of compounds with high boiling points.

Comparing the number of theoretical plates, n (Table II), of the substance under the chosen conditions, it appears that the most efficient column is that containing ST-DMN, although the Chromosorb 101 column is only slightly interior. Much lower n values are obtained for the Porapak Q column. A more complete evaluation of the separability of the columns in relation to the given mixture was made on the basis of $R^i_{,j}$ for the closest pair of in the given mixture of isomers of aliphatic alcohols. The $R_{i,j}$ values were highest for the ST-DMN packing, which accounts for its highest selectivity in relation to alcohol isomers. The short analysis times for the discussed
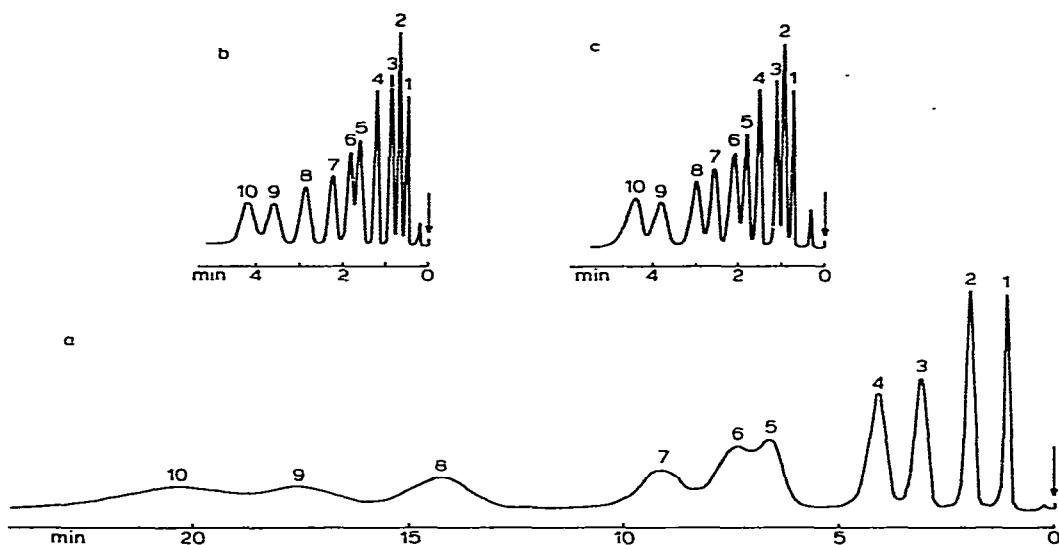
Fig. 1. Comparison of chromatograms of alcohols on Chromosorb 101 (a), Porapak Q (b) and ST-DMN (c). Column: 100 cm × 4 mm I.D., stainless steel; temperature 150°C. Hydrogen flow-rate: 50 ml/min. Injector temperature: 250°C. Catharometer, current: 200 mA. Peaks: 1 = methanol; 2 = ethanol; 3 = propanol-1; 4 = propanol-2; 5 = butanol-2; 6 = 2-methylpropanol-1; 7 = butanol-1; 8 = pentanol-2; 9 = pentanol-3; 10 = pentanol-1.

mixture on Chromosorb 101 and on ST-DMN packings (about 5 min) in contrast to Porapak Q (about 25 min) are of interest (Fig. 1). ST-DMN packings were also found useful for separation of hydrocarbons, ketones, aliphatic acids and amines. In the case of amines, it appeared that on Porapak Q and Chromosorb 101 the heavier amines were adsorbed so strongly that the analysis of the mixtures could not be performed, while on ST-DMN it is possible to obtain a separation of selected amines in a short time (Fig. 2).

In order to evaluate the character of the retention of various classes of compounds on the polymers discussed, the dependences of log V_m on the number of carbon atoms, n_c in molecules of homologous series are used (Figs. 3–9). It appears from Figs. 3–5 that aliphatic n-hydrocarbons, ketones and alcohols have the lowest retentions (under the same measurement conditions) on ST-DMN, while the highest values are found on Porapak Q. Carboxylic acids (Fig. 6) however, are more strongly retained on ST-DMN than on Chromosorb 101. A lower retention at the highest
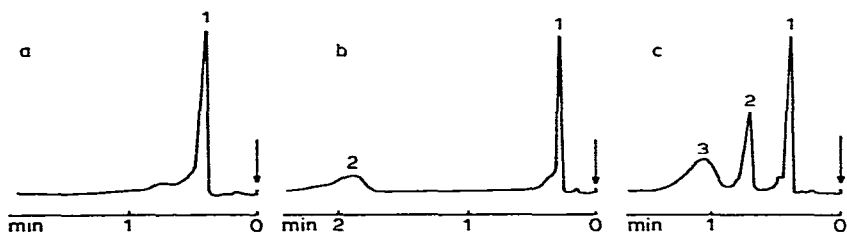

Fig. 2. Comparison of chromatograms of amines on: Chromosorb 101 (a), Porapak Q (b) and ST-DMN (c). Column temperature: 180°C. Other conditions as in Fig. 1. Peaks: 1 = ethylamine; 2 = diethylamine; 3 = triethylamine.
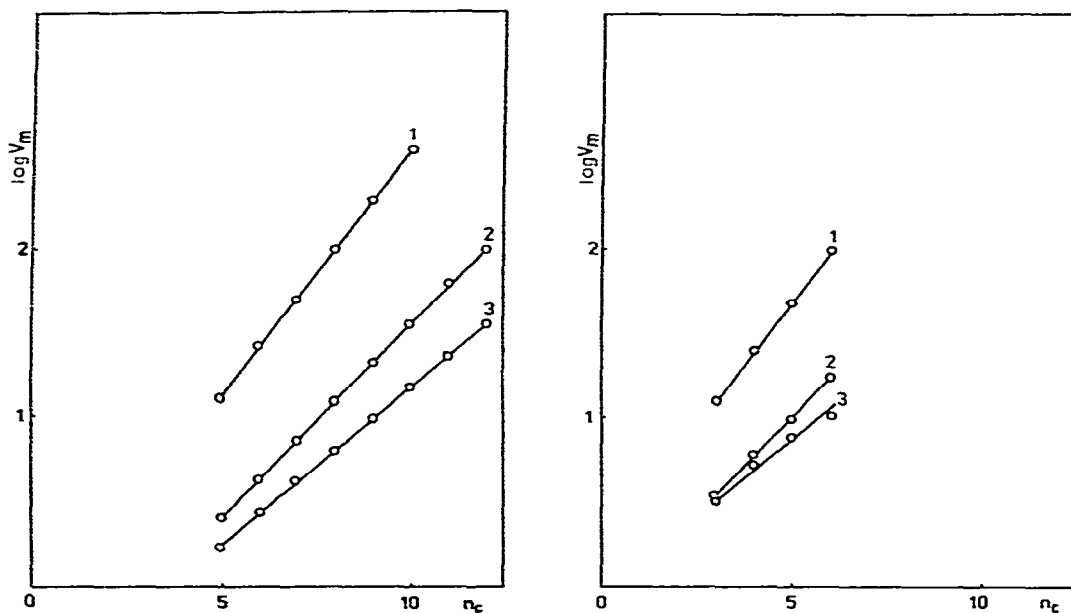
Fig. 3. Dependence of log V_m on number of carbon atoms. n_c, for a mixture of the aliphatic n-hydro-carbons on Porapak Q (1), Chromosorb 101 (2) and ST-DMN (3). Chromatographic conditions as in Fig. 2.

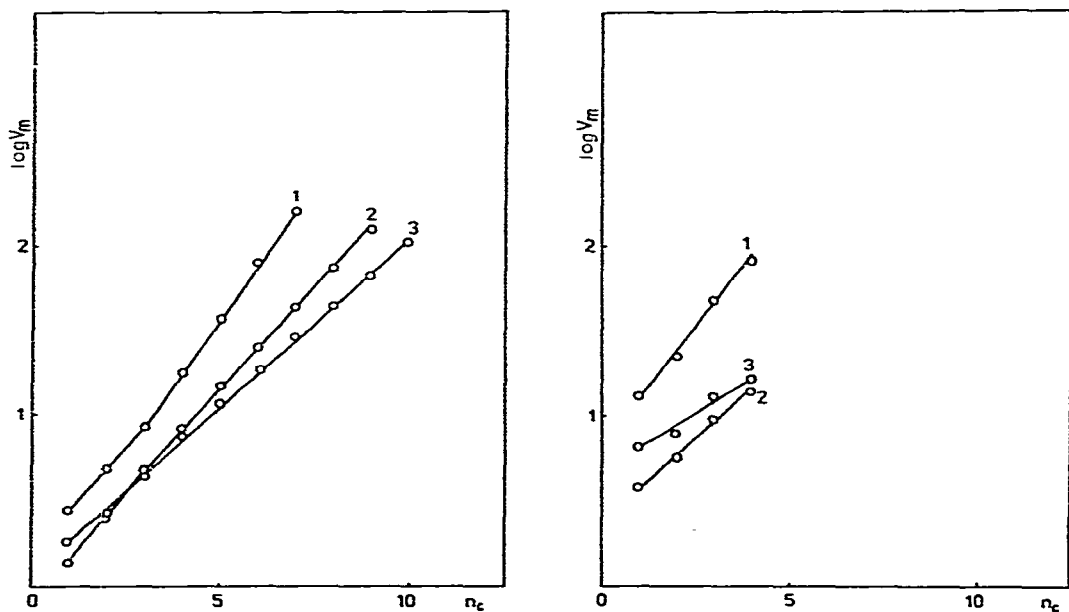Fig. 4. Dependence of log V_m on n_c for a mixture of ketones. Details as in Fig. 3.

Fig. 5. Dependence of log V_m on n_c for a mixture of alcohols. Details as in Fig. 3.

Fig. 6. Dependence of log V_m on n_c for a mixture of n-aliphatic carboxylic acids. Details as in Fig. 3.
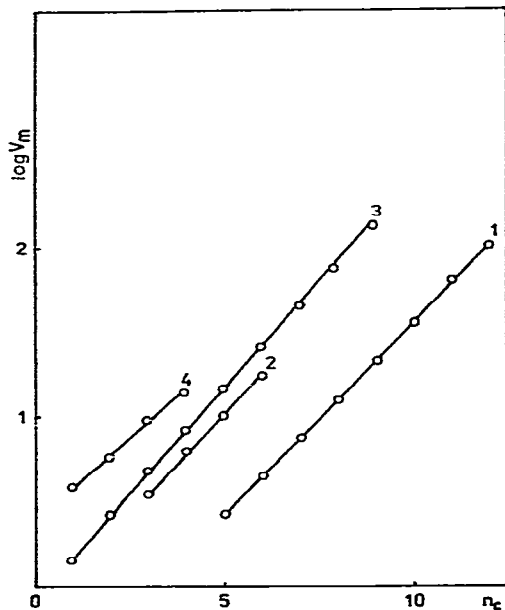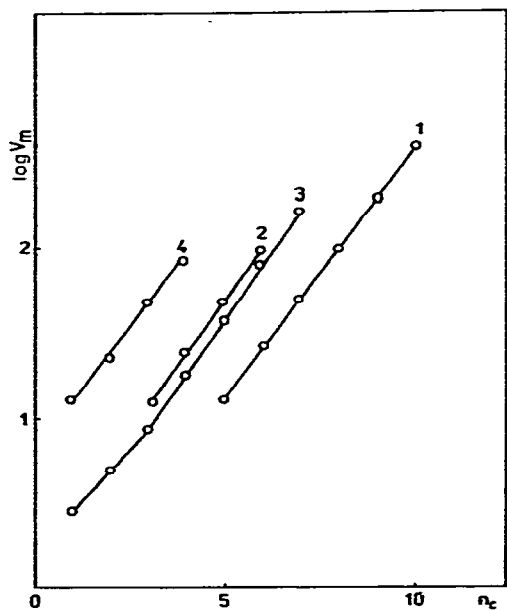
Fig. 7. Dependence of log V_m on n_c for various classes of compounds on Porapak Q: 1 = alipathic n-hydrocarbons; 2 = n-alcohols; 3 = n-ketones; 4 = aliphatic n-carboxylic acids. Chromatographic conditions as in Fig. 2.

Fig. 8. Dependence of log V_m on n_c for various classes of compounds on Chromosorb 101. Details as in Fig. 7.
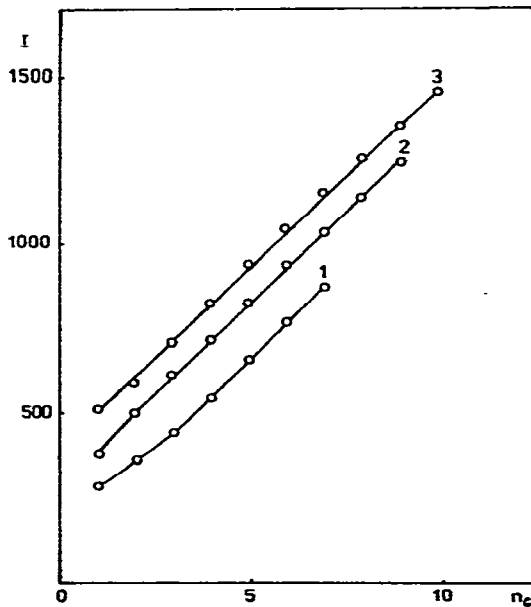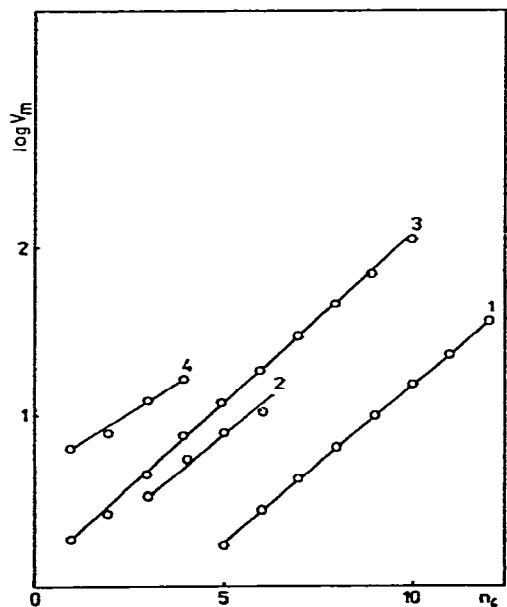

Fig. 9. Dependence of log V_m on n_c for various classes of compounds on ST-DMN. Details as in Fig. 7.

Fig. 10. Dependence of retention index I on n_c for n-aliphatic primary alcohols on Porapak Q (1), Chromosorb 101 (2) and ST-DMN (3). Chromatographic conditions as in Fig. 2.

efficiency and resolution results in the best separation on ST-DMN in the shortest time.

The retention sequence on Porapak Q (Fig. 7; n-hydrocarbon, alchols, ketones, carboxylic acids) was found to be different from that on Chromosorb 101 and ST-DMN (Figs. 8 and 9; n-hydrocarbons, ketones, alcohols, carboxylic acids). This is connected with the non-polar character of Porapak Q, on which strongly polar alcohols are eluted prior to less polar ketones. Further evidence of the high polarity of ST-DMN is the dependence of the retention index on the number of carbon atoms (Fig. 10) for n-aliphatic primary alcohols. The curve for ST-DMN contains the highest values and is also the most linear, creating the most favourable conditions for application of the retention index to identification of substances.

From the increasing distances between the log V_m vs. n_c lines in Figs. 7–9, the selectivity of the packings for various compound classes increases in the order Porapak Q, Chromosorb 101 and ST-DMN.

CONCLUSIONS

The porous polymer ST-DMN shows favourable properties as a packing in gas chromatography. In comparison to Porapak Q and Chromosorb 101, it has the highest initial decomposition temperature and columns prepared from it have the highest efficiency and separability.

It is suitable for the analysis of various compound classes, hydrocarbons, ketones, alcohols and carboxylic acids, and in contrast to Porapak Q and Chromosorb 101, for amines too. Among the porous polymers studied it has the highest polarity, which is associated with the presence of ester groups in the polymer skeleton. Despite this high polarity, it is characterized by the lowest retention for the particular compound classes, which results in shorter analysis times.

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