STUDIES OF CHROMATOGRAPHIC PACKINGS COMPRISING POROUS POLYMERS

I. SORPTION PROPERTIES OF POROUS STYRENE POLYMERS LATTICED BY DI(METHACRYLOYLOXYMETHYL)NAPHTHALENES

T. MATYNIA, A. WAKSMUNDZKI, Z. KONARZEWSKI and M. JARONIEC

Institute of Chemistry, M. Curie-Sklodowska University, Nowotki 12, 20031 Lublin (Poland)

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SUMMARY

The adsorption properties of porous styrene polymers prepared with di-(methacryloyloxymethyl)naphthalenes as the latticing medium have been studied with a view to their utility in the preparation of chromatographic packings for gas and liquid chromatography. Nitrogen adsorption and desorption isotherms have been constructed to calculate the specific surface area, pore-size distribution, mean pore radius and the t curve for different samples of these porous polymers. The surface properties of the samples investigated have been analyzed with respect to the synthesis conditions.

INTRODUCTION

A large number of papers have been published on the problem of obtaining good quality chromatographic packings. Current studies include the improvement of the preparation of already known chromatographic packings and the development of new packings. Great possibilities for the preparation of new chromatographic packings exist with chemically bonded phases[1–4] and the polymerization of organic compounds[5,6]. The application of porous polymers as chromatographic packings shows much promise. In this case there are unlimited possibilities for the synthesis of new kinds of packings (of defined porous structure and chemical nature of the surface). The majority of the known porous polymer packings were prepared on the basis of styrene with divinylbenzene[5,6]; this last compound influences the formation of porous structures in the packing, and is termed the latticing medium.

In this paper, particular consideration is given to the synthesis of porous polymers from styrene and the new latticing medium, a mixture of 1,4- and 1,5-di(methacryloyloxymethyl)naphthalenes. The specific surface area, pore-size distribution and t curves are calculated to characterize the surface properties of the prepared samples. These physicochemical studies are useful in the determination of the optimum conditions for the synthesis of such porous polymers, which may be used

as chromatographic packings for gas chromatography (GC) and liquid chromatography (LC).

EXPERIMENTAL

Reagents

    Materials used for the synthesis of the porous polymers were as follows: styrene (chemically pure; Polskie Odczynniki Chemiczne, Gliwice, Poland), mixture of the isomers 1,4- and 1,5-di(methacryloyloxymethyl)naphthalenes having a fusion temperature of 110–113 °C (obtained from the reaction of a dichloromethyl derivative of naphthalene[7] with potassium methacrylate according to ref. 8; methacrylic acid was obtained from Reachim, Moscow, U.S.S.R.), vinyl polyalcohol (stabilizer), benzil superoxide (initiator), toluene (obtained from Polskie Odczynniki Chemiczene) and *n*-dodecane (Reachim).

Synthesis of the porous polymer

    In a 1-l three-necked flask supplied with a mixer, back-coder and thermometer, 7 g of vinyl polyalcohol were dissolved in 350 ml of water and heated for 2 h at 80 °C. Then a freshly prepared mixture of styrene, a mixture of 1,4- and 1,5-di(methacryloyloxymethyl)naphthalenes, benzil superoxide, toluene and *n*-dodecane (in the proportions given in Table I) was poured slowly into the flask. The resulting mixture was heated under reflux at 80–85 °C for 24 h. The polymer formed was filtered off under reduced pressure and washed several times with hot water (1 l) and then with cold water (200 ml). To remove the stabilizer, suspension, solvents and unlatticed low-molecular-weight polymer, the product was repeatedly extracted with boiling benzene (5 × 100 ml), boiling methanol (5 × 100 ml), boiling acetone (5 × 100 ml) and then again with benzene (2 × 100 ml). The polymer was dried for 2 h at 50–60 °C under a pressure of 4 mmHg and then for 2 h at 150 °C under atmospheric pressure. The above synthesis was very similar to that described in ref. 9.

Measurement of adsorption and desorption isotherms

    Nitrogen adsorption and desorption measurements were performed, at 78 °K,

TABLE I

COMPOSITION OF REACTION MIXTURES USED IN THE SYNTHESIS OF POROUS POLYMERS

Samples	A	B	C	D	E	F
Styrene (*a*), g	30	20	20	9	9	9
Mixture of 1,4- and 1,5-di(methacryloyl-oxymethyl)naphthalenes (*b*), g	10	10	10	10	10	10
Toluene (*c*1), g	34.7	34.7	26	34.7	34.7	52
n-Dodecane (*c*2), g	15	15	11.3	7.5	9	7.5
Weight ratio [*b*/(*a* + *b*)], %	25	33.3	33.3	52.6	52.6	52.6
Volume ratio						
[(*c*1 + *c*2)/(*a* + *b* + *c*1 + *c*2)], %	59.2	66.5	59.8	73.5	74.3	79.5
Volume ratio [(*a* + *b*)/(*c*1 + *c*2)], %	68.8	50.3	67.1	36	34.6	25.7
Weight ratio [(*a* + *b*)/(*c*1 + *c*2)], %	80.5	60.4	80.4	45	43.5	31.9

TABLE II

SORPTION PARAMETERS FOR SAMPLES OF POROUS POLYMERS

S = Specific surface area; C = BET constant; D = standard deviation for BET plot; R_m = pore radius at maximum pore-size distribution; (R_1, R_2) = interval of R for which the pore size-distribution is $> 5 \cdot 10^{-4}$.

Sample	S (m^2/g)	C	$D \cdot 10^4$	R_m (Å)	(R_1, R_2)	$R_2 - R_1$
A	17	220	7.64	120	90–210	120
B	54	82	1.13	260	100–370	270
C	54	82	0.80	180	70–360	290
D	67	71	0.86	140	40–230	190
E	87	76	0.64	160	50–370	320
F	73	152	1.85	140	30–290	260

on the porous polymers by the volumetric method using a Sorptomatic 1806 instrument (Carlo Erba, Milan, Italy). The samples were first vacuum degassed (below 0.005 mmHg) for 2 h at 150 °C. The surface area was calculated by the BET method, using 16.2 Å^2 as the area of coverage per nitrogen molecule. The adsorption and desorption isotherms, and the pore-size distributions, were calculated from the Sorptomatic data according to Barrett et al.[10] and Wheeler[11].

The measurement of the specific surface area of sample B was carried in two ways: in the first case the sample was degassed for 2 h at 150 °C; in the other case the sample was degassed for 4 h at 150 °C. The difference between the measurements of the specific surface area was less than 2 m^2/g, i.e., $< 4\%$.

RESULTS AND DISCUSSION

In Table II, the specific surface area, S, BET constant, C, the standard deviation for the BET plot, D, pore radius at maximum pore-size distribution, R_m, and the
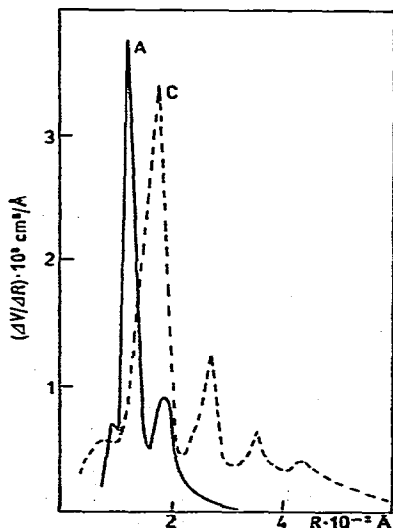

Fig. 1. Pore-size distributions characterizing the samples A (solid line) and C (dashed line).

interval of R for which the pore-size distribution is $> 5 \cdot 10^{-4}$ cm³/Å are summarized for all the investigated samples. Fig. 1 shows the pore-size distributions for sample A (solid line) and C (dashed line). The pore-size distributions for other samples are very similar to those shown in Fig. 1. (The distribution for sample D is similar to that of A; however, the distributions for samples B, E and F are similar to that of C.) All the functions have one distinct maximum and may be approximated by a quasi-gaussian function. The small peaks are probably associated with the method of differentiation of the experimental points.

From Tables I and II certain conclusions can be drawn which might be helpful in the preparation of porous polymers for chromatography. It appears that the surface area of the samples investigated (solid line in Fig. 2) increases with increasing percentage content of the latticing medium [expression $b/(a+b)$ in Table I]. The dependence of the radius R_m on $b/(a+b)$ is more complex (dashed line in Fig. 2). In the region of higher values of $b/(a+b)$ an increase in the surface area S and decrease in R_m is observed; in this case the increase in surface area may be due to a decrease in pore size. In this region a change in the percentage content of the latticing medium does not result in considerable changes in the porous structure of the polymer, but it does affect the pore sizes. It is more difficult to explain correlations of this type in the region of lower values of $b/(a+b)$. In this case a change of the structure of the porous lattice is possible [with increasing $b/(a+b)$, S and R_m both decrease].
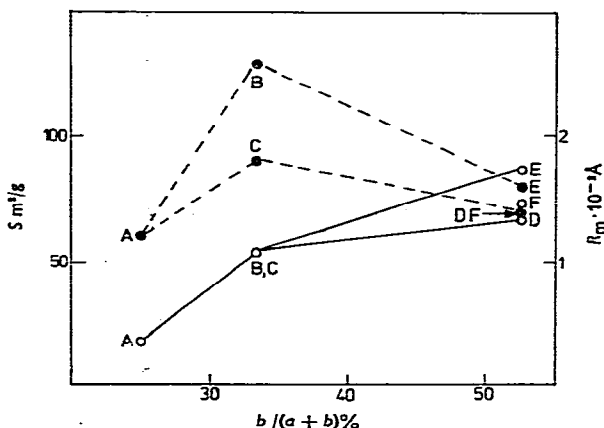

Fig. 2. Dependences of the specific surface area S (solid line with white circles) and the pore radius R_m (dashed line with black circles) on the weight ratio $b/(a + b)$.

Fig. 3 shows the dependence of S and R_m on the weight percentage, $(a+b)/(c1+c2)$. For the first three points (samples D, E and F) the expression $b/(a+b) = 0.526$, whereas for other points B and C the expression $b/(a+b) = 0.333$. These results indicate that a change in the quantity of solvents $(c1+c2)$ does not have a significant effect on the value of the specific surface area; however, it effects the formation of the porous structure.

Packings for adsorption chromatography should be characterized by a homogeneous porous structure, which does not contain micropores. The presence of micropores, causes a deterioration in the quality of chromatographic packings[12]. The
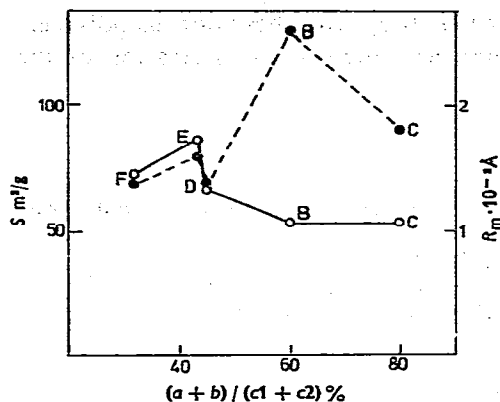
Fig. 3. Dependences of the specific surface area S (solid line with white circles) and the pore radius R_m (dashed line with black circles) on the weight ratio $(a + b)/(c1 + c2)$.

studies carried out here indicate that the porous polymer samples tested do not possess a micropore structure. Fig. 4 shows t curves[13] for samples B, C, D, E and F, plotted with respect to sample A, which may be considered as nonporous (specific surface area 17 m²/g). The calculated t curves are straight lines passing through the origin, which is characteristic for adsorbents without micropores.

At the present stage of the experiments on porous polymers prepared from styrene and di(methacryloyloxymethyl)naphthalenes, the following conclusions can be drawn: (i) the values of the specific surface area of the prepared samples are > 50 m²/g, when the percentage content of the latticing medium, $b/(a+b)$, is in the interval 30–50%; (ii) the dependence of the porous structure of these packings on the
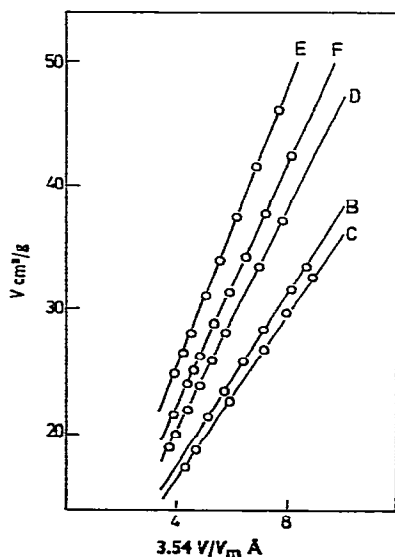

Fig. 4. Dependence of the amount adsorbed, V, on the thickness of the film calculated for samples B, C, D, E and F. The thickness of nitrogen film, equal to 3.54 V/V_m (where V_m is the monolayer capacity), was calculated by using the adsorption data for sample A.

synthesis conditions is complex and requires further study; (iii) these porous polymers have a relatively homogeneous porous structure, and there is no indication of the existence of micropores.

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