A study of the adsorption properties of the hypercross-linked polystyrene sorbents Styrosorb by gas chromatography. Effect of the conditioning temperature

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The effect of the conditioning temperature of the hypercross-linked polystyrene sorbents Styrosorb on the retention of n-hexane, benzene, and acetone was studied by gas chromatography. The rigid but mobile structure of 100% cross-linked polymers with a specific surface area of $300-500$ m^2 g^{-1} prepared in cyclohexane slightly shrinks by conditioning above 200 °C. This results in a significant increase in the specific retention volumes of the adsorbates. The commercial hypercross-linked sorbents MN-100 and MN-200 with specific surface areas of ~1000 m^2 g^{-1} retain their structure up to 250 °C.

Key words: Styrosorb, hypercross-linked polystyrene, parameters of porous structure, gas chromatography, specific retention volume, conditioning temperature.

Macroporous polymeric sorbents are used in gas chromatography not only as the materials for analytical columns but also as concentrators of trace organic substances in air or water. In typical macroporous structures, the substances analyzed are generally adsorbed on the external surface of the tightly cross-linked and impermeable polymeric microphase. However, the adsorption capacity of porous polymers is significantly enhanced when the polymeric microphase gets an intrinsic porosity. Such a structure is typical of Styrosorb hypercross-linked polystyrene sorbents. Some properties of Styrosorbs crucial for their application in gas chromatography have been described previously.[1-4] In this work, we concentrate on the effect of thermal pretreatment of sorbents on the retention of volatile organic substances.

Experimental

The properties of four samples of hypercross-linked sorbents were studied. Sample ST-100-CH-1 (1, Table 1) was prepared by cross-linking polystyrene with a molecular weight of $3 \cdot 10^5$ by monochlorodimethyl ether (0.5 mole per mole of polystyrene) in cyclohexane (CH) in the presence of 1 mole $SnCl_4$ per mole of the cross-linker. The nominal extent of cross-linking of the product was 100%. Its adsorption and chromatographic properties have been described previously.[3] Sample ST-100-CH-2 (2, see Table 1) was prepared in the same way as Sample 1 but in the presence of 2 moles $SnCl_4$. Sample MN-100 (3, see Table 1) is a hypercross-linked sorbent produced by Purolite International Ltd. (Great Britain)

on an industrial scale under the trade mark Macronet Hypersol MN-100 and is characterized by the presence of tertiary amino groups (0.2—0.4 mg-equiv. g^{-1}). Sample 4 is a laboratory analog of the commercial sorbent MN-200 and contains no amino groups.

As can be seen in Table 1, all the samples are characterized by bimodal pore size distribution. They contain micropores and mesopores whose sizes vary over a wide range.

The adsorption properties of sorbents were studied by gas chromatography. Columns of ~30 cm length and 2 mm inner diameter and an Avtokhrom chromatograph with a flame-ionization detector were used. The weighed portions of sorbents were

Table 1. Parameters of the porous structure of the sorbents

Sample	Sorbent	S^a	$W_s^{b,c}$	Pore size/nm	
		/m^2 g^{-1}	/cm^3 g^{-1}	x_0^d	$r^{e,f}$
1	ST-100-CH-1	330	0.6^b	—	4^e
2	ST-100-CH-2	480	0.4^b	1.4	2^e
3	MN-100	1000	0.5^c	0.9	50^f
4	MN-200	1050	—	0.8	50^f

[a] The internal surface estimated from the low-temperature adsorption of Ar or N_2.
[b,c] The volume of the adsorption space determined from the adsorption isotherms of perfluor-n-octane[b] or n-pentane,[c] in which these adsorbents do not swell, in fact,[2] at $p/p_0 = 0.9-1.0$.
[d] Micropore sizes x_0 (a half-width in the slit-like model)[5] calculated from the adsorption isotherm of N_2.
[e,f] Mesopore radii determined from the adsorption isotherms of perfluor-n-octane[e] and by the mercury porosimetry method.[f]

0.20—0.25 g; the grain diameter was 0.16—0.20 mm. N_2 was the carrier gas, and the pressure drop in the column varied from 0.5 to 1.0 atm depending on the temperature. The vapor probes were introduced by a microsyringe. Benzene, *n*-hexane, and acetone were used as adsorbates, and the specific retention volumes $V_{g,1}$ were determined.[6] The $V_{g,1}$ values were measured at various rates of the carrier gas (from 20 to 60 cm^3 min^{-1}). The $V_{g,1}$ value was shown to be practically independent of the rate of the carrier gas, *i.e.*, equilibrium was achieved in fact in the micropores of the sorbents at high temperatures.

Sorbents were conditioned in the column in a flow of N_2 at the temperatures of 100, 125, 135, 150, 175, 200, 225, 250, 275, and 300 °C (time of conditioning was ~3 h). After each step of heating, the column was cooled to 100 or 150 °C and the $V_{g,1}$ values for benzene, *n*-hexane, and acetone were measured. When the column was conditioned at 100, 125, and 135 °C, the measurements were carried out only at 100 °C.

Results and Discussion

It has been shown previously[3,4] that when the $V_{g,1}$ values were measured at 150 °C and above, the chromatographic peaks for organic substances on Styrosorbs were symmetrical and the retention time did not depend in fact on the weight of the sample. At a small dose of an adsorbate, only the adsorbate—adsorbent interaction is manifested in the system, and at equilibrium, the $V_{g,1}$ value is equal (or proportional) to Henry's constant.[6] Hence, the specific retention volume estimated experimentally can serve as an objective characteristic of the adsorption activity of an adsorbent.

Figure 1 presents the specific retention volumes for benzene and *n*-hexane as functions of the specific surface areas S of the samples studied. A point A on these curves corresponds to the retention of adsorbates on the micropore sorbent ST-100-DCE-1[2] synthesized similarly to ST-100-CH-1 but in dichloroethane. As can be seen, the retention volumes of benzene and *n*-hexane for the biporous sorbents prepared in cyclohexane and the microporous polymer ST-100-DCE-1 are proportional to S; however, this proportionality is not obseved for the commercial hypercross-linked sorbents MN-100 and MN-200 with $S \geq 1000$ m^2 g^{-1}. Apparently, the biporous sorbents of the MN series have smaller micropores than Styrosorbs with $S < 1000$ m^2 g^{-1} and are characterized by enhanced adsorption potential. An
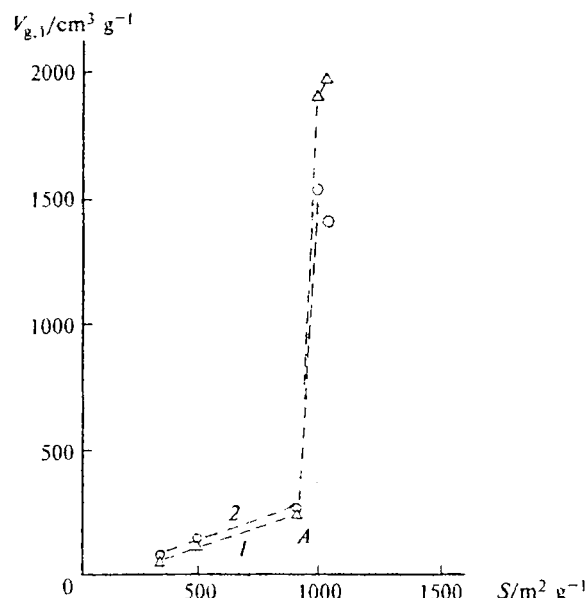

$V_{g,1}/cm^3$ g^{-1}

Fig. 1. Specific retention volumes ($V_{g,1}$) of *n*-C_6H_{14} (*1*) and C_6H_6 (*2*) at 150 °C as a function of specific surface areas (S) of Styrosorbs (point A concerns microporous sample with $S = 910$ m^2 g^{-1}).

increase in the adsorption potential in micropores is more pronounced for *n*-hexane.[7] This conclusion is confirmed by the fact that the adsorption isotherm for *n*-pentane on MN-100 [8,9] at low relative pressures is higher than that on ST-100-DCE-1.[10] A smaller size of micropores in MN-100 and MN-200 (see Table 1) is likely due to the fact that the extent of cross-linking of these sorbents exceeds 100%. It is possible that the entropy factor is also important for adsorption on these polymers.

Differences in the porosity of sorbents affect substantially their chromatographic properties. To monitor the influence of the conditioning temperature of Styrosorbs in a wide range of temperatures (from 100 to 300 °C), $V_{g,1}$ for samples ST-100-CH-1 and ST-100-CH-2 were measured at 100 °C. The chromatographic peaks are broad at this temperature; therefore the findings presented in Table 2 are averages of multiple

Table 2. Specific retention volumes ($V_{g,1}/cm^3$ g^{-1}) of adsorbates at 100 °C on sorbent Styrosorbs conditioned at various temperatures

Adsorbate	100 °C	125 °C	150 °C	175 °C	200 °C	250 °C	275 °C	300 °C
			ST-100-CH-1 sorbent					
n-C_6H_{14}	366	275	300	370	451	566	597	879
C_6H_6	479	400	430	501	602	820 ·	898	1187
$(CH_3)_2CO$	147	82	101	123	151	171	170	188
			ST-100-CH-2 sorbent					
n-C_6H_{14}	1230	1123	1062	1076	1137	1371	1528	1731
C_6H_6	1359	1292	1238	1294	1358	1562	1644	1836
$(CH_3)_2CO$	181	178	179	177	189	204	216	245

measurements at different sample volumes. As can be seen in Table 2, sorbent ST-100-CH-2 retains all adsorbates more strongly than ST-100-CH-1. This is likely due to the larger specific surface area of the polymer prepared in the presence of a greater amount of the catalyst and by the smaller mesopore size. Benzene is characterized by high thermodynamic affinity for polystyrene and is retained by both sorbents more strongly than *n*-hexane.

As seen in Table 2, an increase in the conditioning temperature of sorbents from 100 to 125 °C results in lowering the $V_{g,1}$ values for adsorbates; then the $V_{g,1}$ values change slightly in the range of 125—175 °C and increase substantially with further increase in the conditioning temperature of the column from 200 to 300 °C.

In order to corroborate the effect of increasing the retention values $V_{g,1}$ in the temperature range of 200—300 °C, we repeatedly measured $V_{g,1}$ at 150 °C with another column, which was packed with sorbent ST-100-CH-2. As follows from Fig. 2, the effect of increasing the $V_{g,1}$ values for all adsorbates is reproducible. We assumed that at temperatures >200 °C, the strongly retained molecules of the solvent are removed from the polymer and additional sorption space appears. Usually, after the chemical reaction has been completed, the catalyst and the solvent immiscible with water are removed by washing with acetone, methanol, and water and then the polymers are dried at 80—100 °C. The replacement of an organic solvent by water
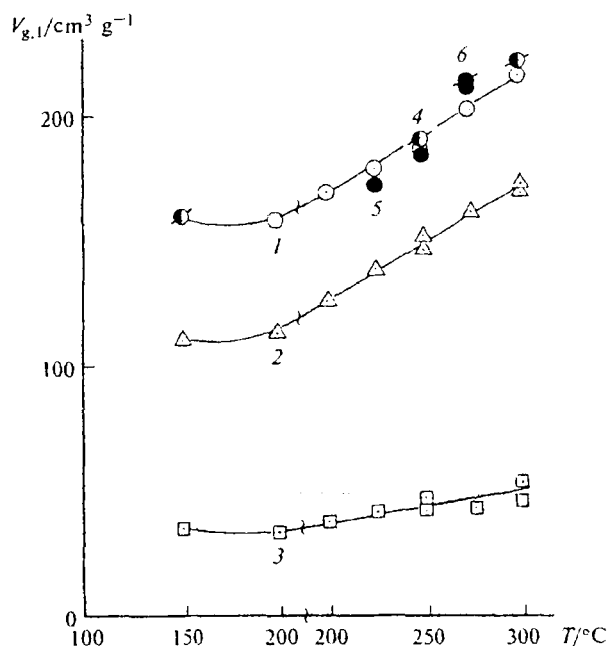
and the following drying are accompanied by pronounced shrinkage of polymers and their significant internal straining due to deformation of a number of rigid bridges. Such a state of the hypercross-linked polymer is the least favorable thermodynamically. Therefore, the hypercross-linked polymer can strongly retain in the extremely strained positions the solvent molecules, which can be removed only at high temperatures. It is also possible that the samples were insufficiently washed and dried prior to the chromatographic testing.

To verify these assumptions, we carried out two additional series of runs with this sorbent. In one case, a new portion of sorbent ST-100-CH-2 was repeatedly washed with acetone, methanol, and water and dried at 150 °C. As seen in Fig. 2, the $V_{g,1}$ values for benzene remained the same after additional purifying. The findings for *n*-hexane and acetone were similar. In another case, sample ST-100-CH-2 was saturated with methanol at room temperature after conditioning at 275 °C, and excess methanol was removed at 150 °C; then the retention volumes of the adsorbates were measured at 150 °C. If the methanol molecules were again adsorbed in the most strained positions of the polymer network, the $V_{g,1}$ values would be reduced. However, as Fig. 2 shows, this is not the case. It remains to suggest that at temperatures above 200 °C, some irreversible conformational rearrangements occur in the rigid but mobile hypercross-linked network with 100% extent of cross-linking, which are accompanied by additional shrinkage of the structure and decrease in the micropore size. They remain accessible for the adsorbates chosen, but their adsorption potential increases and the specific retention volumes increase. It seems that the decrease in the micropore sizes is not so high and does not significantly affect the internal specific surface area of sorbents. The specific surface areas of polymer ST-100-CH-2 before heating and after long heating at 300 °C are equal to 490 and 510 m² g⁻¹, respectively.

A suggestion on shrinking the polymers during conditioning is indirectly confirmed by the data of Fig. 3.
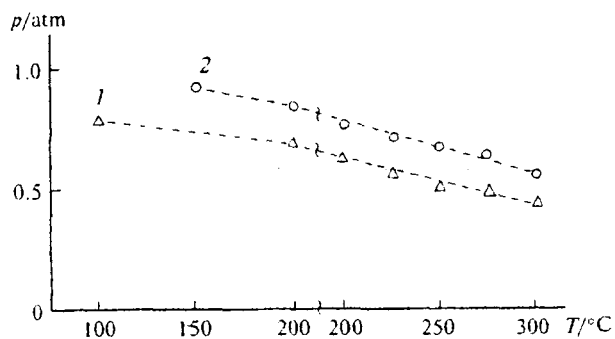
$V_{g,1}/\mathrm{cm}^3\ \mathrm{g}^{-1}$

Fig. 2. Specific retention volumes ($V_{g,1}$) of C_6H_6 (*1*, *4—6*), *n*-C_6H_{14} (*2*), and $(CH_3)_2CO$ (*3*) at 150 °C as a function of the conditioning temperature for sample ST-100-CH-2: the sample without additional washing, the first loading (*1—3*), the second loading (*4*); previously washed sample (*5*); the sample presaturated with methanol at room temperature (*6*).

p/atm

Fig. 3. The pressure (*p*) at the inlet of the column at a constant rate of the carrier gas of 40 cm³ min⁻¹ and a temperature of the column of 100 (*1*) and 150 °C (*2*) as a function of the conditioning temperature of the column with sorbent ST-100-CH-2.

Table 3. Specific retention volumes ($V_{g,1}/cm^3 g^{-1}$) of adsorbates on sorbent Styrosorbs conditioned at various temperatures

Adsorbate	200 °C	225 °C	250 °C	275 °C	300 °C
	Sorbent MN-100 (T_{col} = 200 °C)				
n-C_6H_{14}	421	—	402	—	335
C_6H_6	340	—	340	—	315
$(CH_3)_2CO$	100	—	100	—	86
	Sorbent MN-200 (T_{col} = 175 °C)				
n-C_6H_{14}	379*; 813	823	809	745	—
C_6H_6	301*; 616	632	626	612	—
$(CH_3)_2CO$	57*; 101	102	101	97	—

* T_{col} = 200 °C.

It is proved that at constant temperature and flow rate of carrier-gas (40 cm^3 min^{-1}), an increase in the conditioning temperature of a column results in a decrease in the pressure drop. This fact can be rationalized only by a decrease in the size of the polymer particles and irregular packing of the sorbent particles in the column.

The hypercross-linked Styrosorbs MN-100 and MN-200 differ in properties from Styrosorbs prepared in cyclohexane (samples 1 and 2). The retention of organic substances by MN-100 and MN-200 is significantly higher than that by samples 1 and 2 (see Fig. 1). Therefore, to study the effect of the conditioning temperature of these sorbents on their adsorption capacity, the $V_{g,1}$ values of the adsorbates used were measured at 200 °C for MN-100 and 175 °C for MN-200. As seen in Table 3, these sorbents are extremely stable. Conditioning at temperatures up to 250 °C exerts no effect on the values of the retention volumes. A tendency of the $V_{g,1}$ values to decrease is observed only upon conditioning at temperatures above 250 °C. Even such rigid networks are likely shrunk at these temperatures, and the fraction of micropores becomes inaccessible to the molecules under study.

Styrosorbs MN-100 and MN-200 retain more n-hexane than benzene (see Table 3). The micropores in these sorbents are likely more accessible for a flexible hydrocarbon molecule than to a rigid aromatic ring, and the observed difference in the retention volumes is due to the molecular-sieve effect.

The higher values of $V_{g,1}$ for n-hexane and benzene on sample MN-100 as compared to sample MN-200 are likely due to the presence of micropores of smaller size in sample MN-100. The markedly higher $V_{g,1}$ values for

acetone (100 cm^3 g^{-1} *vs.* 57 cm^3 g^{-1}) (see Table 3) are caused by specific interaction of the acetone molecules with Styrosorb MN-100, which contains tertiary amino groups.

Thus, gas chromatography proved to be a very sensitive method, which allows one to reveal fine changes in the internal structure of a polymeric sorbent caused by high temperatures. The method gives qualitative evidence for the difference in the sizes of micropores in Styrosorbs synthesized under different conditions and regimes of conditioning.

Hypercross-linked sorbents MN-100 and MN-200 are stable at high temperatures and retain volatile organic substances. The findings obtained in this work show that these sorbents are suitable for concentrating trace contaminants in air followed by their thermal desorption.

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