Structure and properties of porous hypercrosslinked polystyrene sorbents 'Styrosorb'

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<u>Abstract</u> – Hypercrosslinked sorbents "Styrosorb" were obtain-
ed by introducing large number of rigid bridges between li-
near polystyrene chains in solution or in a highly swollen
state. This crosslinking procedure results in a homogeneous
network which appears to be highly porous when in dry state.
The porosity stems from the loose packing of polymer chains
in the rigid network. The inner specific surface area of
Styrosorbs, when calculated formally in terms of the BET
theory, reaches a value of 1000–1300 m^2/g, though a more de-
tailed analysis reveals the failure of the theory to describe
the sorbtion ptoperties of the polymers. The total volume of
voids does not exceed 0.5 cm^3/g, with an average pore diame-
ter of 1.0–1.5 nm. However, the inner surface of the sorbents
appears to be easily accessible to both small and large or-
ganic molecules due to a cooperative conformational rearran-
gement of the network under the influence of the sorbate mo-
lecules. The sorption capacity of Styrosorbs with respect to
vapours of organic compounds exceeds by far the capacity of
known types of polymeric and inorganic sorbents. Styrosorbs
efficiently extract non-polar organic compounds from aqueous
and polar organic media. They are further useful as column
packing materials in size exclusion chromatography of oligo-
mers.

INTRODUCTION

Numerous polystyrene-derived sorbents are widely used in modern technology.
Some of them are based on conventional or gel-type styrene-divinylbenzene
(DVB) copolymers that are obtained by a copolymerization reaction carried
out in the absence of any diluter. These products are homogeneous and non-
porous when in dry state, and they can only be used in media causing a
strong swelling of their network. Well known Dowex ion exchangers are syn-
thesized from such gel-type copolymers. Another type of network, macropo-
rous one, results from a copolymerization procedure of styrene with a large
portion of DVB, which is carried out with a diluter that precipitates the
growing polystyrene chains. Porosity of materials thus obtained reflects
the phase segregation during the synthesis. Any solvent can fill in the
macropores without causing a noticeable swelling of the polymeric phase
that is highly crosslinked. Sorbents Amberlyte XAD-2 and XAD-4 represent a
typical example for macroporous structures.

The present paper deals with hypercrosslinked polystyrene sorbents Styro-
sorb which possess a principally different structure and offer therefore
new possibilities for sorption procedures from gaseous and liquid media.

SYNTHESIS AND STRUCTURE OF STYROSORBS

Instead of a traditional copolymerization of mono- and divinyl monomers,
crosslinking of high-molecular-weight polystyrene chains in solution or in
a highly swollen state is the distinguishing feature of the synthesis pro-
tocol for the Styrosorb networks. Bifunctional reagents such as 4,4'-bis-
(chloromethyl)biphenyl (CMB) (Ref. 1), p-xylilene dichloride (XDC) (Ref. 2),
monochlorodimethyl ether (MCDE) (Ref. 3), or dimethyl formal (DMF) (Ref. 4)

are used to crosslink polystyrene in accordance to the Friedel-Craft's reaction. In this case, a bridge between two polymeric chains forms the following structure:
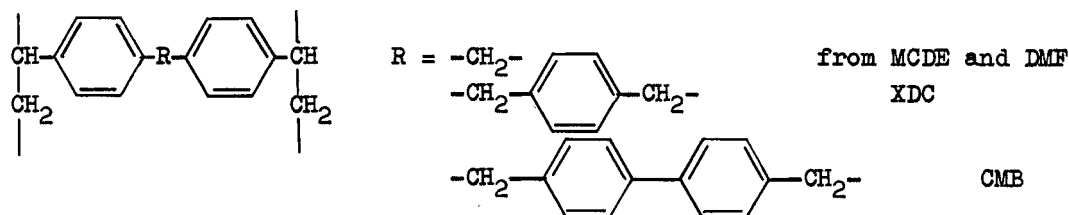
The bridges have limited conformational mobility with the diphenylmethane link produced by MCDE and DMF being the most rigid one.

To prepare type I Styrosorb materials, linear atactic polystyrene with an average molecular weight of 300000 was taken as the initial polymer. Its volume-concentration in the homogeneous solution of all components of the reaction in dichloro ethane amounted to 10-11%. Due to crosslinking, the initial solution is converted into a swollen gel, which is finally broken up to produce Styrosorb I particles of an irregular shape. To obtain spherically-shaped Styrosorb II sorbents, beads of styrene copolymers with 0,3-2% DVB are subjected to crosslinking with MCDE in a highly swollen with dichloro ethane state. In all the reactions, $SnCl_4$ served as the condensation catalyst.

The content of cross bridges in the network can be easily changed by varying the amount of the crosslinking reagent, since the consumption of the latter in the reaction was shown to be quantitative. Therefore, the crosslinking degree of the network can be defined and estimated as the fraction of cross bridges in the total sum of structural elements comprising the cross bridges and unsubstituted phenyl groups. If 0,5 mol of a bifunctional reagent is involved in reaction with 1 mol of polystyrene, practically all the initial phenyl rings should be incorporated into cross bridges in the final polymer, and the crosslinking degree of the latter would be 100% (Ref. 5). In practice, networks with crosslinking degree of 40% or higher display some unusual properties, which requires their treatment as a separate class of polystyrene networks, a hypercrosslinked one.

Crosslinking polystyrene chains in the presence of large amounts of a good solvent does not cause any microphase segregation and results in the formation of a homogeneous swollen network (Ref. 5). Removing the solvent from the gel is always accompanied by conformational rearrangements of polymeric chains, the latter seeking to attaine a dense packing. Because of the high content of rigid crosslinks, a dense packing in a hypercrosslinked network cannot be attained. The structure remains loose, which manifests itself in a low density of the material and the highly developed inner surface area.

It should be emphasised that the contraction of the network during the removal of the solvent from the hypercrosslinked gel necessarily results in the development and rapid growth of inner strains in the network. These strains remain unrelaxed in the dry material and they facilitate the swelling of the latter in any media, even those that prove to be unable to dissolve linear polystyrene or cause swelling of weakly crosslinked styrene copolymers. To put the explanation the other way round, the polymer-polymer interactions in the hypercrosslinked network appear to be so low that even a relatively weak solvation of polystyrene chains with solvents like methanol or hexane would already produce a dramatic increase in the volume of the network (Ref. 6).

SORPTION OF GASES AND VAPOURS ON HYPERCROSSLINKED SORBENTS STYROSORBS

In spite of the fact that dry Styrosorb particles are glassy and fully transparent to the light, they adsorb large amounts of inert gases. Adsorption isotherms for nitrogen and argon at -196°C are S-shaped and produce a straight line in coordinates of the Brunauer-Emmet-Teller equation in the range of relative pressures p/p_0 from 0 to 0,35. Formally, this justifies the application of the BET theory to calculating the inner specific surface area, S_{sp}, of the sorbents (Table 1).

TABLE 1. Apparent values of inner specific surface area S_{sp}, m^2/g, of Styrosorbs I and II, as determined by the method of thermal desorption of argon

Network Type	DVB %	Cross agent	Total crosslinking degree, %				
			11	25	43	66	100
I	–	MCDE	0	240	650	1000	1000
I	–	XDC	0	100	500	800	1000
I	–	CMB	0	100	670	800	1000
I	–	DMF	0	250	600	750	1000
II	0.8	MCDE	0	120	–	1000	1350

It follows from Table 1 that true porosity is only characteristic of hypercrosslinked structures and here, it can reach surprisigly high values. Rigid networks of both types I and II with crosslinking degrees of 60–100% withstand heating to 100–150°C for several hours without changing their inner surface area values. That the rigidity of the network is essential for the polymers to display true porosity, can be corroborated by the fact that products of polystyrene crosslinking with a conformationally flexible di(chloromethylphenyl)butane-1,4, $ClCH_2C_6H_4-(CH_2)_4-C_6H_4CH_2Cl$, never adsorb inert gases, irrespective of the degree of crosslinking. Furthermore, they do not swell in methanol and hexane (Ref. 7).

Contrary to the exceptionally high values of specific inner surface area, the total pore volume of Styrosorb was found to be moderate. It is remarcable that the pore volume W_o^{N2} determined from the nitrogen adsorption isotherms at $p/p_o \sim 1$ and –196°C appears to be substantially higher than the pore volume W_o^P calculated from the difference in the apparent and true densities of the material (Table 2). This situation is only feasible when the sorbent swells in vapours of nitrogen (Ref. 8).

TABLE 2. Total pore volume, cm^3/g, of Styrosorb I crosslinked with MCDE

Crosslinking degree, %	W_o^P	$W_o^{N_2}$	W_o^{Hg}
43	0.36	0.45	0.24
66	0.44	0.54	0.39
100	0.51	0.68	0.48

Table 2 also contains values W_o^{Hg} of pore volume obtained from mercury porosimetry experiments (Ref. 9). This method provides, in addition, information on pore diameters. In the present case, however, pore diameters thus obtained amounted to 20–60 nm (irrespective of the crosslinking density), which differed from the results of other methods. Thus, inverse size exclusion chromatography (Ref. 10) could not reveal pores larger than 5–7,5 nm in swollen Styrosorb I and II gels and located a sharp maximum of the pore diameter distribution curve at 1.0–1.5 nm. Electron microscopy does not permit detecting any morphology elements in Styrosorb II beads. These polymers do not scatter X-rays under small angles (Ref. 11). Obviously, their loose network merely undergoes compression under mercury, which is experimentally indistinguishable from the intrusion of mercury into pores of 20–60 nm in diameter.

Results of a detailed examination of sorption properties of Styrosorb polymers appear confusing, as well (Table 3). Sorption isotherms of water and carbon dioxide at room temperature and nitrogen and argon at -196°C are S-shaped and exhibit a distinct hysteresis loop. A linear relation in coordinates of the BET-equation is followed throughout the usual range of p/p_0 values in the case of sorption of water vapour, but merely up to $p/p_0 =$ $= 0.018$ in the case of nitrogen sorption at 20°C. There is no correlation between the calculated capacity, a_m, of the monomolecular adsorption layer

and the point B on the adsorption isotherm for CO_2. Whereas on rising the degree of crosslinking the surface chemistry of the sorbent should not change much, the constant C in the BET equation was found to fall by a factor of 4 in the case of sorption of water and to rise by an order of magnitude in the case of sorption of CO_2 (Table 3). Finally, there is a dramatic

difference between the values of inner surface area estimated with respect to different sorbates. All these contradictions lead to a conclusion that there is no constant solid surface in the hypercrosslinked polymer that is exposed to the sorbates.

TABLE 3. Adsorption parameters of Styrosorb I crosslinked
         with XDC (Ref. 12)

Crossl. degree, %	Adsorbate	Temp. °C	S_{sp} m²/g	Point B	BET constants a_m	C
43	H_2O	20	7	–	0.081	32
	CO_2	20	90	0.50	0.687	301
	N_2	-196	258	2.10	2.640	95
	Ar	-196	530	–	–	–
66	H_2O	20	9	–	0.103	19.5
	CO_2	20	92	1.30	0.701	3601
	N_2	-196	442	3.40	4.530	111
	Ar	-196	820	–	–	–
100	H_2O	20	14	–	0.16	7.9
	CO_2	20	100	1.40	0.761	2158
	N_2	-196	673	5.70	6.90	146
	Ar	-196	956	–	–	–

Adsorption of argon on Styrosorbs was found to be especially high. With respect to this sorbate, the hypercrosslinked polymers behave in such a manner as if their inner surface area amounted to 1000 m²/g.

Adsorption isotherms of nitrogen at room temperature are quite remarcable (Fig. 1). There is a distinct hysteresis loop on all the isotherms. Further, whereas the maximum sorption capacity at room temperature is exhibited by the sorbent having a degree of crosslinking of 43%, there is a steady increase in the sorption capacity with the growing degree of crosslinking when measurements are made at -196°C using Ar (Table 1) or N_2 (Ref. 12).

Fig. 2 represents a sorption isotherm of water vapours on a Styrosorb II crosslinked to a degree of 100%. The isotherm has a classical S-shape, though for hydrophobic surfaces and activated charcoal-type sorbents the isotherm should be rather concave (type III of the BDDT classification).

Again, the above results lead to a conclusion that there is a marked change in the inner structure of the polymer taking place under the influence of the sorbate.

In fact, a straightforward experiment on Styrosorb II beads unambigously shows that an increase in the sorbent volume accompanies the sorption process and it starts long before the initial void volume of the polymer (0.22 cm³/g) is filled out with the sorbate. Sorbate molecules entering the
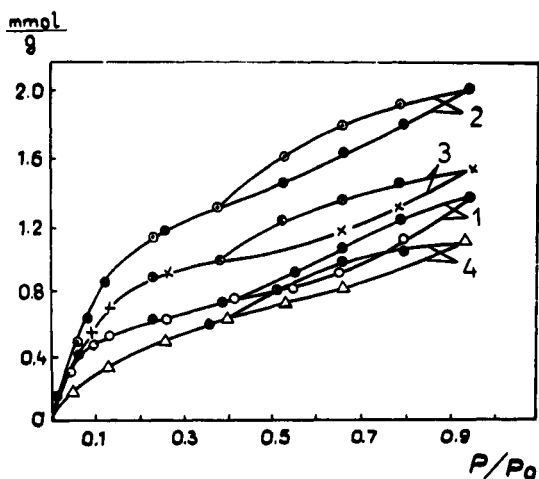
Fig. 1. Sorption and desorption iso-
therms of nitrogen at 20°C on Styro-
sorb I crosslinked with XDC to an ex-
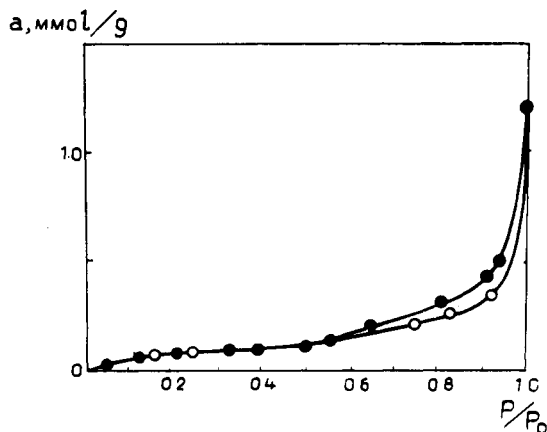tent of 20 (1), 43 (2), 66 (3), and
100% (4). p_o = 760 mm Hg.

Fig. 2. Sorption (o) and desorption
(•) isotherms of water vapour on
Styrosorb II, obtained by crosslinking
styrene-0.7 DVB copolymers to an
extent of 100%.

sorbent network cause an immediate increase in its volume, thus providing
more void space for the subsequent sorption. Therefore, in spite of the fact
that the initial void volume in the hypercrosslinked polymer is relatively
small, the total sorption capacity of the polymer with respect to vapours
of, e.g., n-hexane (Fig. 3) exceeds by far the capacity of such known ad-
sorbents as zeolyte NaX, activated charcoal AR-3 or macroporous styrene-DVB
copolymer Polysorb 40/100. From a practical viewpoint it is also important
that the regeneration of Styrosorbs does not require much of energy. It
easily proceeds in vacuum or on heating the sorbent to 80°C (Ref. 14).
Contrary to this, activated charcoals release n-hexane only at 200-350°C.

An interesting feature of hypercrosslinked polystyrene sorbents is that
different sorbates produce sorption isotherms of different shapes (Fig. 4),
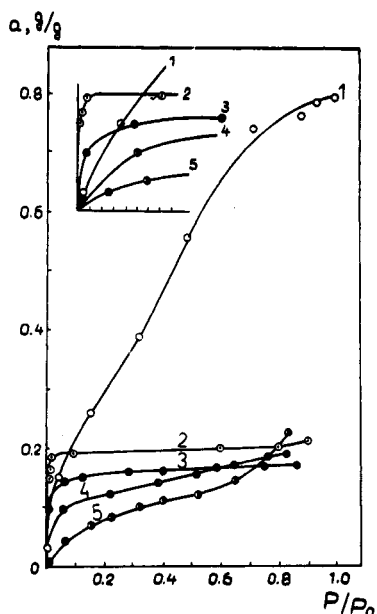

Fig. 3. Sorption isotherms of n-hexa-
ne vapours at 20°C on Styrosorb II (1),
Zeolyte NaX (2), Activated charcoal
AR-3 (3), graphitized coal (4), and
macroporous styrene-DVB copolymer
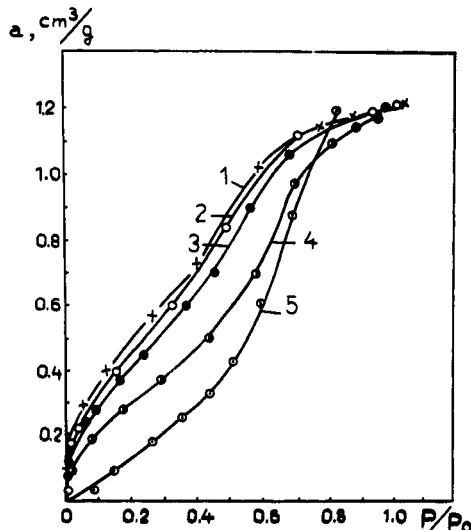Polysorb 40/100 (5).

Fig. 4. Sorption isotherms of vapours
of n-heptane (1), n-hexane (2),
n-pentane (3), acetone (4), and
methanol (5) on Styrosorb II
(0.7x100) at 20°C.

(Ref. 13). Hydrocarbons give isotherms of the S shape, whereas methanol, as a sorbate with strong intermolecular interactions, gives an isotherm that is concave towards the axis of relative pressures. Sorption of n-perfluorooctane is distinguished by slow kinetics (Fig. 5). Obviously, the shape of the isotherm is generally determined by a superposition of physical adsorption and polymer swelling phenomena, rather than porous structure of the material.
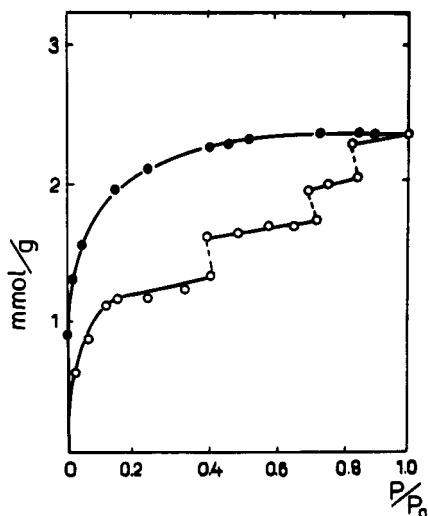

Fig. 5. Isotherms of sorption (o) and desorption (•) of vapours of perfluorooctane on Styrosorb II (0.7x100) at 25°C.
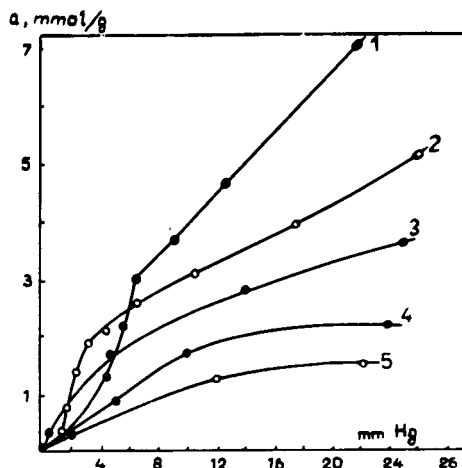
Fig. 6. Sorption isotherms of n-hexane vapours on Styrosorb II (0.7x100) at temperatures 0 (1), 10 (2), 20 (3), 40 (4), and 60°C (5).

At relative pressures approaching $p/p_0 = 1$, Styrosorbs take up almost equal quantities of vapours of different organic solvents, with the exception of perfluorocarbons. As this takes place, the equilibrium values of swelling in saturated vapours never reach completely the swelling values in the corresponding liquids. We explain this interesting observation by the surface tension on the gel/vapour interface being higher than that on the gel/liquid interface, which results in different compression forces that the tension exerts on the gel particles.

Temperature dependence of adsorption of vapours by the hypercrosslinked polystyrene was also found to be unusual. It follows from Fig. 6 that in the range of small p/p_0 values, adsorption of n-hexane at 0°C appears to be lower than that at higher temperatures. Obviously, lowering the temperature to 0°C results in freezing some kind of mobility of the polymer network, which diminishes or slows down the swelling process of the latter.

Structure of Styrosorb I preparations synthesized in cyclohexane appears to be heteroporous. Even at elevated temperatures, from the thermodynamic point of view this solvent is not as good to polystyrene as is dichloroethane. When polystyrene of a molecular mass of 300000 is subjected to crosslinking in a solution in cyclohexane, the final product exhibits pores of 4-5 nm in diameter, in addition to usual pores of 1.0-1.5 nm (Ref. 15). The size of the larger pores rises with the molecular weight of the initial polymer decreasing. Thus pores of 20 nm in diameter are characteristic of sorbents prepared from a low-molecular-weight (about 13000) polystyrene (Ref. 16). Hypercrosslinked networks of this type do swell in any liquid and gaseous media, as well. This can be seen (Fig. 7) from the facts that the sorption hysteresis loop occupies the whole range of relative pressures, down to $p/p_0 \sim 0$. and that the maximum quantity of vapours adsorbed exceeds by far the pore volume in the dry polymer. Only perfluorooctane was found to give a hysteresis loop largely similar to typical capillary condensation.
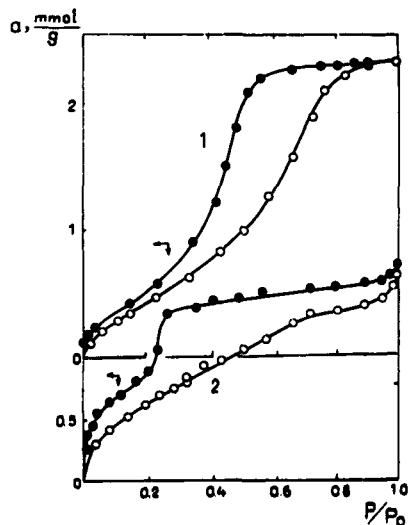
Fig. 7. Sorption isotherms of n-per-fluorooctane vapours at 25°C on Styro-sorbs I obtained by crosslinking poly-styrene of molecular mass of $3 \cdot 10^6$ (1) and $3 \cdot 10^5$ (2) in cyclohexane with MCDE
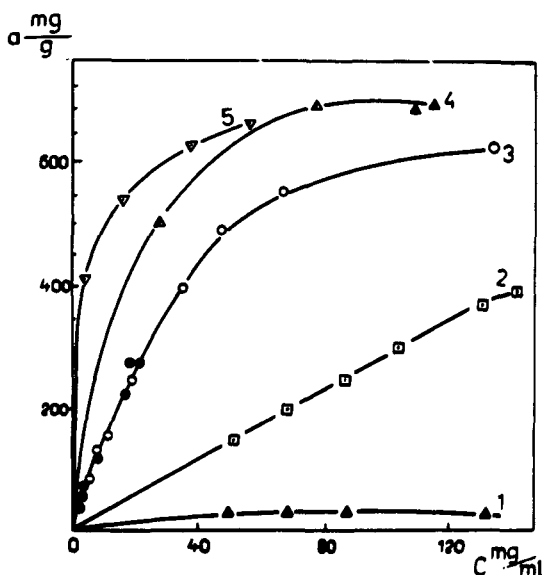
Fig. 8. Sorption isotherms of leci-tine at 20°C on Polysorb 40/100 (1), Amberlyte XAD-4 (2), Styrosorb II (0.7x100) (3-5) from isopropanol (1-3), isopropanol/water mixtures of 4/1 (4), and isopropanol/water mixtures of 1/1 (5).

SORPTION FROM AQUEOUS AND ORGANIC MEDIA

Styrosorbs proved to be excellent adsorbents for many organic substances dissolved in polar liquid media. However, only rarely they can be applied immediately to agueous solutions since water does not wet polystyrene. This obstacle can be easily overcome by wetting the polymer first with acetone, ethanol, or any other organic solvent that is compatible with water and then replacing the solvent with water. In this manner, the sorbent acquires its equilibrium water-swollen state and exhibits fully its sorption ability. Most useful for sorption, concentration and purification procedures are Styrosorb products with the crosslinking degree of 100%.

Fig. 8 illustrates sorption isotherms of lecitine from pure isopropanol and its mixtures with water (Ref. 18). The lipid uptake of Styrosorb amounts to 0.7 g per 1 g of the sorbent which is much higher than the sorption capa-city of the known macroporous polystyrene adsorbent Amberlyte XAD-4.

Superb are sorption properties of cyclohexane-synthesized crosslinked poly-mers as it was shown, for instance, for valeric acid solutions (Ref. 14). Due to the bimodal pore size distribution, these polymers are easily acces-sible to large organic molecules. Thus, 1 gram of Styrosorb I modification that was prepared in cyclohexane absorbs more than 1 gram of high molecular weight dyes, melanoidines, from cultural liquors of microbiological amino acid production plants (Ref. 19). The sorbent can be easily regenerated and used repeatedly in sorption-desorption cycles.

When used as column packing materials for high-performance liquid chromato-graphy, Styrosorb-type polymers offer new and important possibilities, especially when they are employed in the form of monodisperse micro spheres of 3 or 4 μm in diameter. For instance, they proved useful in size exclu-sion chromatography for analysing various oligomers in any kind of organic media. As highly efficient and selective materials for solid extraction, Styrosorb microbeads facilitated an immediate analysis of propranolol and its metabolites in blood plasma by making any laborious solvent extraction or deproteination procedures fully superfluous. Similarly to propranolol behave seduxen, phenaptin, triampur, glaucin and many other important pharmacological drugs.

CONCLUSION

Crosslinking polystyrene chains in solution by means of a large number of rigid cross-bridges results in networks exhibiting non-trivial swelling and sorption properties. Behaviour of the networks is governed by a distinct tendency to acquire the swollen non-strained state which was characteristic of the synthesis product. Therefore, in contrast to all known types of porous adsorbents, adsorption on the hypercrosslinked polystyrene, Styrosorb, is always accompanied, if not superceded, by a swelling process of the polymeric matrix with sorbate.

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