

Utilization of Wastes of Foam Polystyrene as Sorbents

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SYNOPSIS

Wastes of foam polystyrene were dissolved in styrene and copolymerized with DVB and the final product was sulfonated with H_2SO_4 (group B). Group A of cross-linked polystyrene was synthesized using styrene and divinylbenzene (DVB) in the presence of *n*-heptane (macroporous ion exchangers) and then was sulfonated with H_2SO_4 . The chemical structure of the cross-linked polymers before and after sulfonation was determined by infrared spectroscopy. The ion-exchange capacity was higher for the polymers of group A. The pore-size distribution for polymers of group A was determined and the average pore diameter ($4V/A$) of 39.9 nm for a representative polymer resulted. The degree of swelling of the polymers and their adsorption for methylene blue and alizarin yellow were also determined. The degree of swelling in toluene is decreased by increasing the ratio of DVB in the initial mixture and by sulfonation. The adsorption of methylene blue and alizarin yellow is strongly increased by the sulfonated polymers in comparison with the unsulfonated. As far as group B is concerned, the adsorption of alizarin yellow on the sulfonated polymers, which have higher cross-linking and lower sulfonation, increased more, especially at the initial time. The networks of both groups examined are different. The polystyrene wastes were incorporated into the whole network to an extent of 15–35%. Such investigations could contribute to the utilization of wastes of polystyrene in the direction of sorbents and especially if the polystyrene wastes are contaminated with other polymers. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polymers are increasingly used as sorbents, i.e., as materials that absorb or sorb ions and molecules of different substances from various media. They are diverse in ion-exchange resins and polymer sorbents. Ion exchangers contain functional groups with an ion charge (e.g., $R-SO_3H$, $R-COOH$, $R-NH_2$) that form a salt with the counterion in the resin. This counterion can be exchanged by other ions of the same charge, which are contained in the solution. During the exchange process, an equilibrium reaction occurs.¹ On the other hand, for the adsorbent resins, a chemically exact defined group does not react with exactly known equivalents, but a general adsorption of other molecules on the resin takes place. Ion-exchange resins are divided into “standard” or “gel” and “macroporous” according to their

preparation technique. On the other hand, the polymer sorbents are divided in “gel” and “macroporous.”

Both last mentioned resins may contain functional groups that do not give ions (e.g., $R-Cl$, $R-COOR$, $R-SO_2-R$) or do not contain any functional groups at all.^{1,2} In gel sorbents, solution uptake is accomplished primarily by swelling. Macroreticular sorbents are highly cross-linked and macroporous, with pore size in the order of 10^1-10^2 nm, and they uptake solution primarily by pore filling.³ Cross-linked gels of polyelectrolytes, whose pores are defined as the distances between polymeric chains, can be considered as *microreticular*. Contrarily, *macroreticular* resins contain a significant nongel porosity in addition to the conventional gel porosity. The nongel interstices of the styrene-divinylbenzene (St-DVB) macroreticular resins are channels between agglomerates of very small spherical gel particles.⁴ The gel-type resins of the St-DVB type do not contain any true porosity. Ions to be exchanged must be diffused through the gel structure

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to the exchange sites. Macroreticular ion-exchange resins have large discrete pores with an average pore diameter of ca. 130 nm. They offer a number of advantages over the conventional gel-type resins: Their large discrete pores mean that high molecular weight ions can be removed more completely from the solution and eluted more completely from the resin on regeneration than would be in the case of other materials. Furthermore, the open structure of the macroreticular resins permits the use of tough copolymers that would be too dense to act effectively as ion-exchange resins if they were used in a strictly gel-type system. Although the macroreticular resins, on the whole, have a somewhat lower capacity than do the gel-type resins, this is often offset by the longer operating life of the macroreticular resins or the fact that they will effect removals that would be not possible by the gel-type resins.^{4,5}

The synthesis of porous St-DVB copolymers is an attractive subject for many researchers and such products are commercially available.^{2,4,6,7} Ion-exchange resins, as well as adsorbents (e.g., macroporous resin), can be produced by suspension copolymerization of St-DVB. Macroporous resins are produced by copolymerization in the presence of a third component (like *n*-heptane), which does not participate in the reaction and is a good solvent for the monomer and a poor solvent for the polymer.² On the other hand, nowadays, polymer wastes are an important subject of research and development. The recycling or the utilization of polymer wastes saves raw materials and protects the environment. Polystyrene (PS) is one of the three standard plastics (polyolefines, PVC, PS) and the foam products of PS consist a large application field. The aim of this work was to investigate the process of the modification of wastes of foam polystyrene in order to obtain sorbents. The adsorbability of the prepared sorbents was performed on the basis of dye adsorption. Methylene blue (having electron-donor groups) and alizarin yellow (having mainly electron-acceptor groups) were chosen as dyes. The dyes are in aqueous solution without usage of a buffer solution. Such investigations could contribute to the utilization of polymer wastes in the field of the sorbents.

EXPERIMENTAL

Wastes of foam polystyrene (viscosity-average molecular weight of 140,000 determined by dilute solution in toluene) were cut and dissolved in St. The copolymerization with DVB was performed in a 2 L polymerization reactor using free-radical polymerization and a suspension process. Benzoylperoxide

was used as the initiator in the proportion of 1.33% w/w to the mixture of monomers St-DVB and the initial PS. Poly(vinyl alcohol) was used as the suspension stabilizer in the proportion of 1.67% w/w to the aqueous phase. The ratio of the aqueous phase to the organic phase was 4.7. The polymerization was performed at 80°C for 1 h and at 90°C for 2 h under the flow of nitrogen. After filtration, the pearls were washed with distilled water, extracted with methanol, and dried. The sulfonation was performed with concentrated H₂SO₄ (in the presence of Ag₂SO₄) at 100°C for 3 h. The polymers prepared were treated with toluene and then were extracted with methanol and dried and their weight losses determined. The ion-exchange capacity of the sulfonated polymers was also determined.

Furthermore, for comparison reasons, St was copolymerized with DVB in the presence of *n*-heptane following a similar procedure. After the polymerization, the diluent was removed by distillation with steam and the polymer was extracted with methanol and then dried. The polymer was sulfonated as has been previously described.

The infrared (IR) spectra of the unsulfonated or sulfonated polymers were carried out using KBr tablets. The porous structure of the polymers was determined by Hg-porosimetry and the calculation model is based on the cylindrical approach of pores.

The polymers prepared were swollen with toluene at 20°C for 24 h and the degree of swelling α was determined by the gravimetric method according to the following equation²:

$$\alpha = (m_t - m_0) / m_0$$

where m_0 and m_t are the weight of the initial polymer sample and that of the swollen polymer sample at time t during the swelling, respectively.

The adsorption abilities of the unsulfonated and sulfonated polymers were determined from aqueous solutions of two dyes, viz., methylene blue and alizarin yellow R, of initial concentrations 0.0320 g/L. For this determination, a certain amount of the polymer (30 g/L) was mixed with a known amount of an aqueous solution of the dye at 25°C without stirring. The color of the solution was determined after various time intervals by using a colorimetric calibration scale and the colorimeter Lovibond Tintometer Model E.

RESULTS AND DISCUSSION

Table I refers to the polymerization and other processes, like sulfonation, solution, and ion exchange,

Table I Polymerization and Other Processes for the Manufacture of Adsorbents Using Styrene Without or With Wastes of Polystyrene (St: Styrene; PS_w: Polystyrene Wastes; PS_{cr}: Polystyrene Cross-linked, Nondissolved)

Symbol	(Co)polymerization					Sulfonation	Solut. Process PS _{cr} /PS _w (% w/w)	Ion Exchange Capacity (meq/g Dry Res.)
	St (% w/w)	PS _w (% w/w)	DVB (% w/w)	PS _w /St (% w/w)	DVB/St + PS _w (% w/w)			
1	83		17		20	No		
1S	83		17		20	Yes		4.3
2	60		40		66.7	No		
2S	60		40		66.7	Yes		4.9
3	40		60		150	No		
3S	40		60		150	Yes		3.3
1WS	67	10	23	15	30	Yes	20	1.2
2WS	57	20	23	35	30	Yes	35	1.2
3WS	67	23.5	9.5	35	10	Yes	15	2.0
4WS	77		23		30	Yes		1.4

Group A: polymers 1, 2, 3, 1S, 2S, 3S. Group B: polymers 1WS, 2WS, 3WS, 4WS. Ratio of monomers to heptane (V/V): 1.2, 1.7, 0.7, for polymers 1, 2, and 3, respectively.

for the manufacture of adsorbents using St without or with wastes of PS. The polymers prepared by using *n*-heptane during polymerization and then sulfonated (group A) show higher values of ion-exchange capacity than do those prepared without using *n*-heptane and then sulfonated (group B).

Figure 1 shows the IR spectra of a typical cross-linked polymer before and after the sulfonation. The IR bands according to the literature are as follows⁸: The cross-linked polymer [Fig. 1 (a)] shows the following groups: OH (at 3.400–3.200 cm⁻¹), unsaturated and aromatic C—H stretching vibrations (at

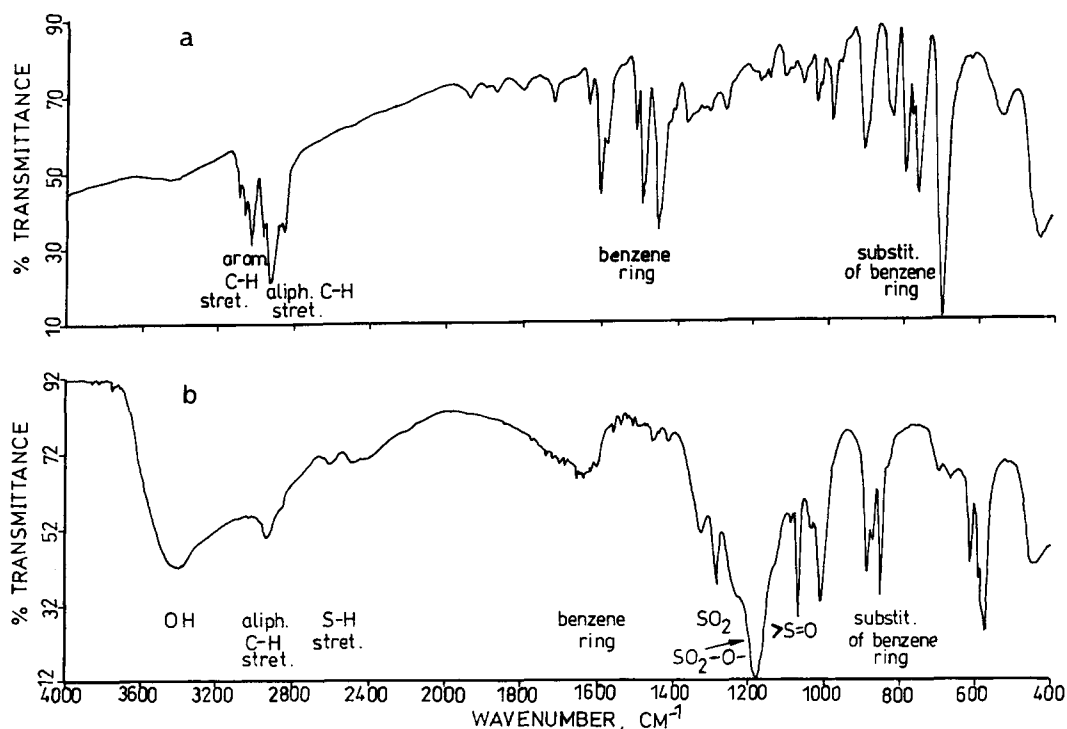


Figure 1 IR spectra: (a) cross-linked PS (polymer 3, see Table I); (b) cross-linked and sulfonated PS (polymer 3S, see Table I).

3.024 cm^{-1}), CH_2 bending vibrations (at 2.922 and 2.850 cm^{-1} , often as two or three bands), $\text{C}=\text{C}$ without conjugation (at 1.601 cm^{-1}), aromatic ring (at 1.492 cm^{-1}), CH_2 (at 1.451 cm^{-1}), $\text{>C}=\text{C}<$ (with two R in *trans*-configuration, at 988 cm^{-1}), various substitutions of the benzene ring between 900 and 770 cm^{-1} (at 903, 795, 759 cm^{-1}), and CH_2 rocking (at 720 cm^{-1}). The cross-linked and sulfonated polymer [Fig. 1(b)] shows the following groups: OH (very strong at 3.600–3.200 cm^{-1}), CH_2 (at 2.926 cm^{-1}), $-\text{S}-\text{H}$ stretching vibrations (at 2.602 cm^{-1} , aromatic ring (at 1.600 cm^{-1}), >SO_2 (at 1.323 and 1.283 cm^{-1}), $-\text{SO}_2-\text{O}-$ (at 1.177 cm^{-1}), $\text{>S}=\text{O}$ (at 1.070 cm^{-1}), and various substitutions of the benzene ring between 900 and 770 cm^{-1} (at 888, 851 cm^{-1}). The various groups of sulfur absorb in the “fingerprint” region (under 1.500 cm^{-1}) (the absorption at 2.600–2.550 of the $-\text{S}-\text{H}$ is very weak).

Figure 2 shows the basic reactions that take place during polymerization, crosslinking, and sulfonation processes. Figures 3 and 4 show the pore-size distribution concerning incremental volume per gram % and incremental surface area per gram %, respectively, for a representative polymer of group A, viz., macroporous ion-exchange resin.² The curve of the incremental volume shows two main maxima, viz., between the pore radius 10^4 – 10^5 nm and lower than 10^1 nm. The curve of the incremental surface area is increased by decreasing pore radius. The porosity features according to these figures are summarized in Table II.

The degree of swelling (Fig. 5) is strongly increased at the beginning of the swelling and then approaches equilibrium. Polymers 1WS and 2WS swell less than does 3WS due to their more dense cross-linkings. Polymer 4WS swells more than do 1WS and 2WS, which have the same ratio of DVB/(St + PS_w). On the other hand, 1WS and 2WS have incorporated 20 and 35% of the initial PS (see Table I, column “solut. process”). That means that the incorporated PS has also been cross-linked, so that the polymers 1WS and 2WS have higher cross-linking than that expected from the initial proportion of DVB. Polymer 3WS incorporates 15% of the initial PS (see Table I); however the proportion of DVB used is lower [DVB/(St + PS_w) = 10%] than that of 1WS, 2WS, and 4WS. Expressing approximately the cross-linking by the sum of DVB/(St + PS_w) and PS_{cr}/PS_w (see Table I), the polymers prepared under the same conditions can be ordered by decreasing cross-linking or degree of swelling:

$$2\text{WS} (65\%) < 1\text{WS} (50\%) < 4\text{WS} (30\%) \\ < 3\text{WS} (25\%)$$

The polymers prepared in the presence of *n*-heptane (group A) follows the order of decreasing degree of swelling:

$$3\text{S} < 2\text{S} < 1\text{S} \ll 3 < 2 < 1$$

This order corresponds to the nominal degree of cross-linking (according to the ratio DVB/St, PS_w = 0, for the above polymers, see Table I) if it is taken into consideration that the unsulfonated and sulfonated polymers are separated groups. The sulfonated polymers show a lower degree of swelling than do the unsulfonated polymers, because the sulfo group has a low affinity to the unpolar toluene.

Figures 6 and 7 represent the adsorption of polymers from aqueous solutions of methylene blue and alizarin yellow, respectively. The adsorption is increased by increasing adsorption time for the corresponding polymers. For methylene blue, the adsorption is increased according to the order of polymers of group B:

$$1\text{WS} > 3\text{WS} > 2\text{WS}$$

(at the beginning and at the equilibrium)

The unsulfonated polymers of group A adsorb very little of both dyes used. The sulfonated polymers adsorb methylene blue according to the order

$$1\text{S} > 3\text{S} > 2\text{S} \text{ (at the beginning)}$$

$$1\text{S} > 2\text{S} > 3\text{S} \text{ (at the equilibrium)}$$

The adsorption of alizarin yellow on the polymers follows the order

$$1\text{WS} > 2\text{WS}$$

> 3WS (for group B, at the beginning).

All polymers adsorb fully at the equilibrium).

3S > 1S > 2S (for group A, at the beginning).

Their adsorption is more as they approach

equilibrium: 3S = 2S > 1S).

It is remarkable that all polymers of group B show higher adsorption than do the polymers of group A for alizarin yellow. Concerning each group separately, the adsorption is increased by increasing cross-linking and decreasing ion-exchange capacity. (Polymer 4WS has an intermediate adsorption within the group B for both dyes.)

The swelling as well as the adsorption on poly-

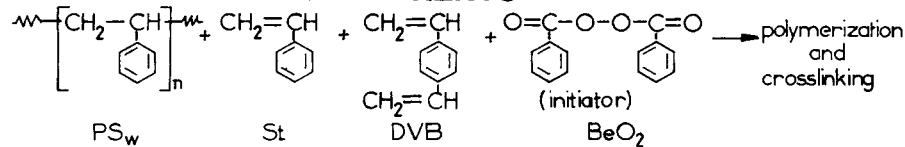
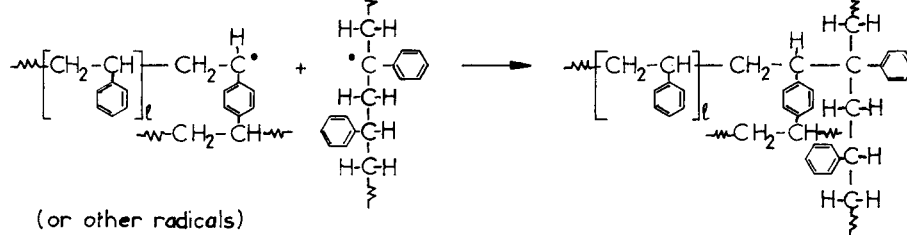
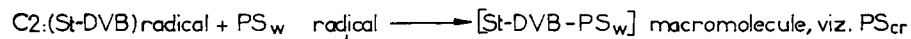
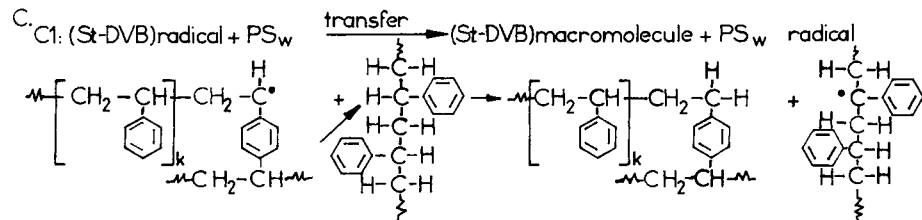
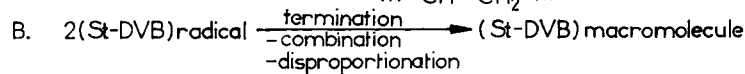
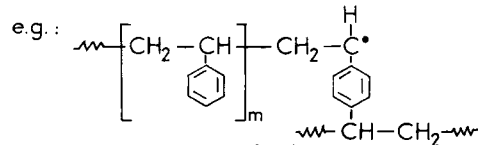
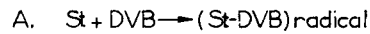
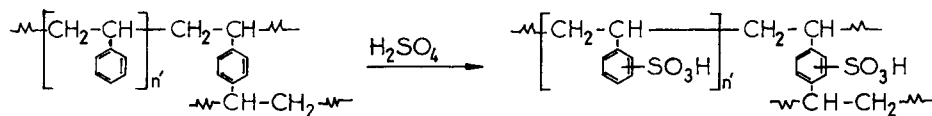
I) BASIC REACTION COMPONENTS

II) POLYMERIZATION AND CROSSLINKING

III) SULFONATION of polymers


Figure 2 Basic reactions taken place during polymerization, cross-linking, and sulfonation processes.

mers are complicated phenomena. During hydration, macroporous St-DVB sorbents show major changes in the pore sizes and their distribution due to the expansion of their matrices as has been determined by transmission electron microscopy using image analysis.⁷ The swelling of such resins is very affected by the solvent used, e.g., methanol or toluene, as well as by the diluent used during the polymerization, e.g., toluene is a solvating diluent of the polymeric chains.⁶ The experimental data of swelling are well correlated to the structure of the polymers, viz., the expected cross-linking is dependent on the preparation conditions and the modification by sulfonation.

On the other hand, the experimental adsorption data cannot be directly correlated to the whole structure of the polymers. However, some general characteristics, which influence the adsorption, can be remarked upon. The adsorption of dyes on porous PS depends on the typical pore characteristics as well as on the shape of pores, which is affected by the preparation method, e.g., suspension polymerization using a nonsolvent of the polymer or dissolution of PS in its solvent and then precipitation using a nonsolvent of the polymer.⁹ The porosity of the polymers of group A does not favor considerably the adsorption of the dyes, e.g., polymers of group B that are prepared by the absence of heptane adsorb

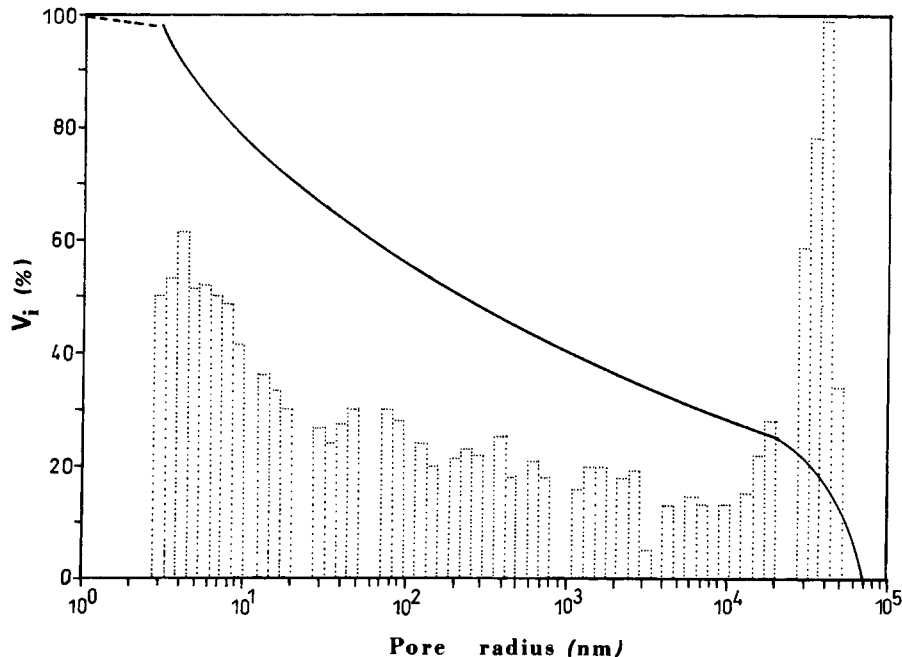


Figure 3 Pore-size distribution of polymer 1 (see Table I). V_i : cumulative pore volume per gram (%).

more alizarine yellow than do the polymers of group A, which are more porous. Furthermore, the porosity cannot be directly correlated to the cross-links. The space between cross-links can be characterized as

pores, but, generally, pores are defined as voids or space between separate grains, layers, crystals, and other elements of the coarse structure of a solid.² Cross-linking aims to make the polymer insoluble

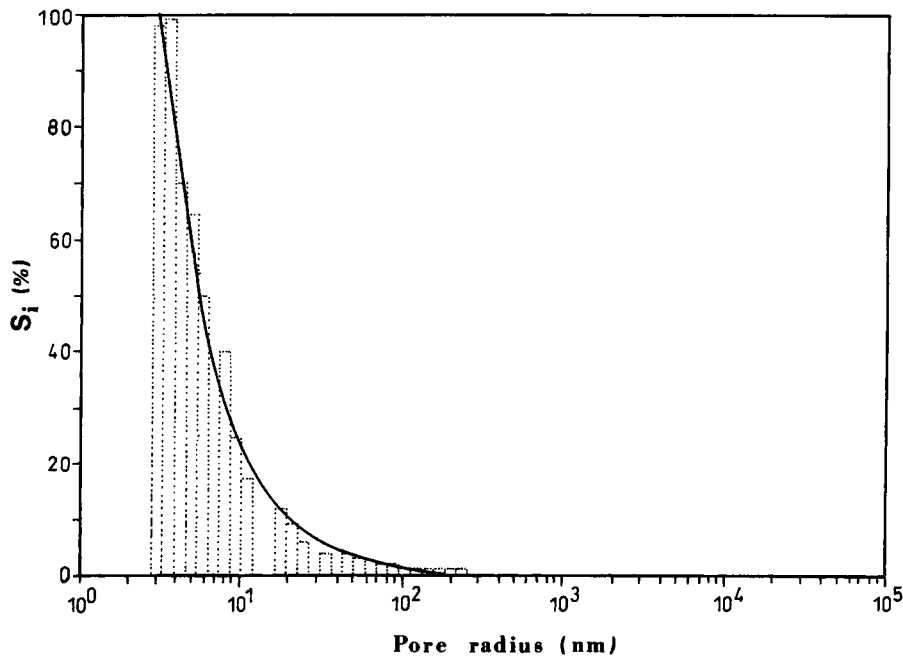


Figure 4 Pore-size distribution of polymer 1 (see Table I). S_i : cumulative surface area per gram (%).

Table II Summarized Data of Porosity and Swelling Features According to Figures 3–5 for Polymer 1 (Table I)

No.	Porosity and Swelling Features of Polymer	Value of Features
1	Maximum incremental volume	0.0175 cm ³ /g
2	Maximum incremental surface area	4.94 m ² /g
3	Total intrusion volume	0.2166 cm ³ /g
4	Total pore area	21.7 m ² /g
5	Median pore diameter (volume)	486.1 nm
6	Median pore diameter (area)	10.6 nm
7	Average pore diameter (4V/A)	39.9 nm
8	Bulk density	0.7378 g/cm ³
9	Apparent (skeletal) density	0.8782 g/cm ³
10	Capillary	34.95%
11	Equilibrium degree of swelling	1.8 w/w

or of limited swellability in solvents, and for this purpose, sorbents and ion exchangers very often have this structure.

The introduction of the functional group in St-DVB resins by sulfonation strongly affect the adsorption of both dyes used. Methylene blue (having electron-donor groups) and alizarin yellow (having mainly electron-acceptor groups) have been successfully used for the characterization of the ad-

sorption ability of acrylic polymers [polyacrylonitrile, poly(acrylic acid), etc.] and the adsorption results are interpreted in terms of electron donor-acceptor (EDA) interactions.^{10,11} The stronger sulfo group (in the case of St-DVB resins) instead of the carboxylic group (in the case of acrylic polymers) seems to act as a typical ion (using such resins as typical ion-exchange resins), not through polar interactions.

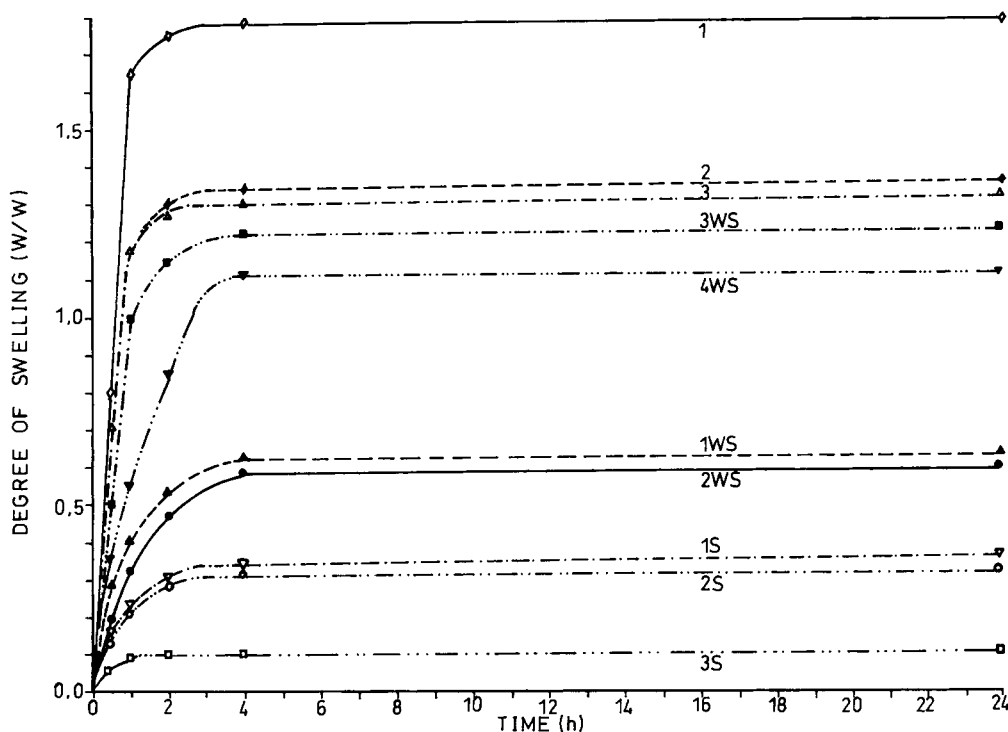


Figure 5 Degree of swelling vs. time (description of symbols: see Table I).

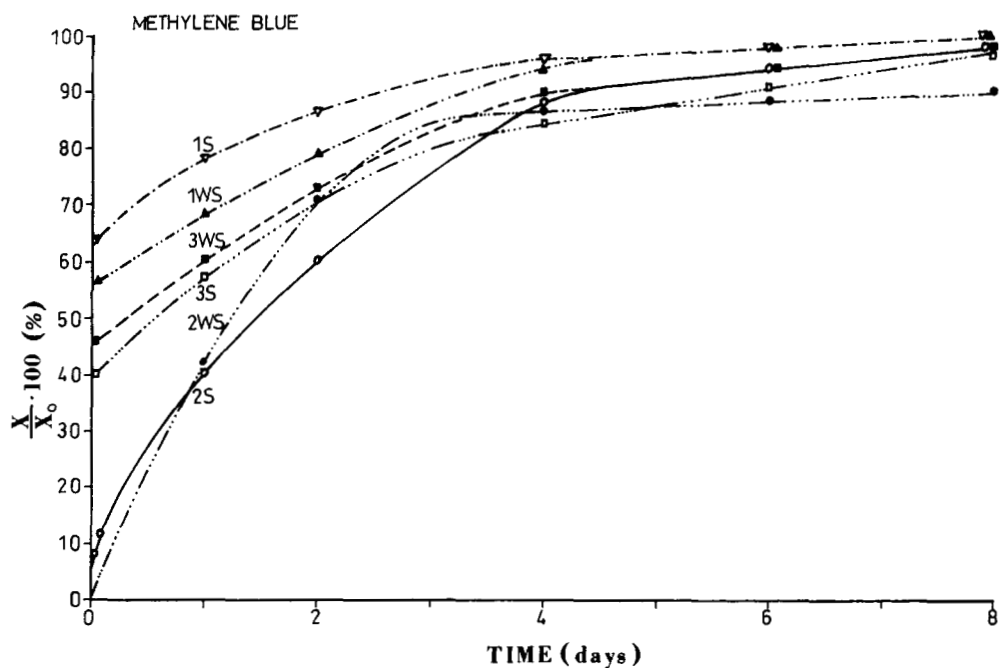


Figure 6 Adsorption of methylene blue from aqueous solution on polymers. The adsorption is referred as $(X/X_0) \times 100$, where X is the adsorbed amount of dye, and X_0 , the initial amount of dye in the solution before the adsorption. Description of symbols: see Table I.

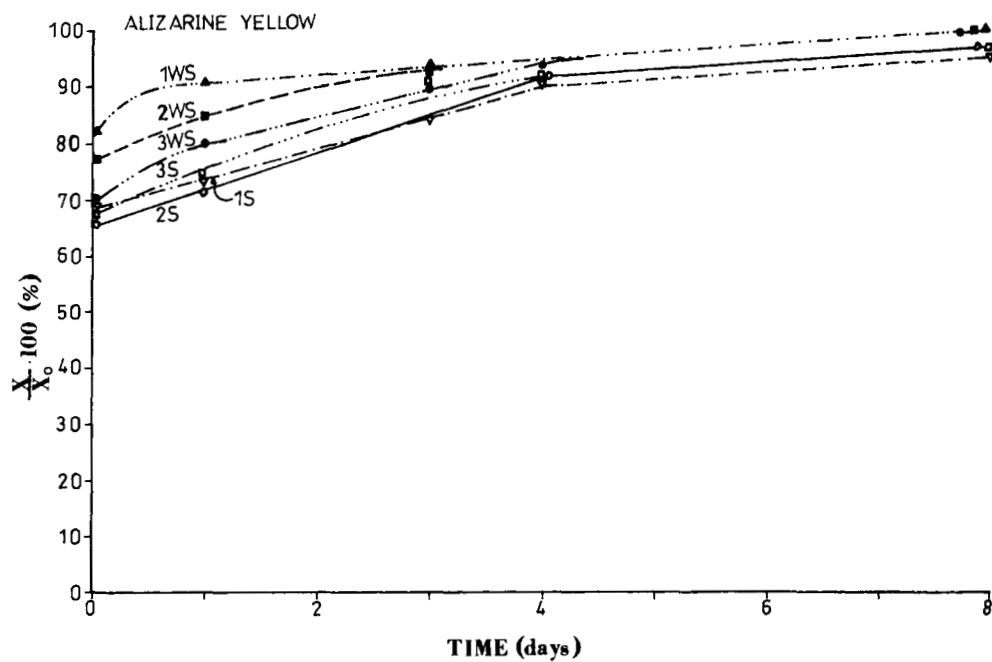


Figure 7 Adsorption of alizarin yellow from aqueous solution on polymers. The adsorption is referred as $(X/X_0) \times 100$, where X is the adsorbed amount of dye, and X_0 , the initial amount of dye in the solution before the adsorption. Description of symbols: see Table I.

CONCLUSIONS

Wastes of foam PS were dissolved in St and copolymerized with DVB and the product was sulfonated with H₂SO₄ (group B). Group A of cross-linked PS was synthesized using St and DVB in the presence of *n*-heptane (macroporous ion exchangers) and then was sulfonated with H₂SO₄. It is concluded that

- The degree of swelling in toluene is decreased by increasing the ratio of DVB in the initial mixture and by sulfonation.
- The adsorption of methylene blue and alizarin yellow is strongly increased by the sulfonated polymers in comparison with the unsulfonated. As far as group B is concerned, the adsorption of alizarin yellow on the sulfonated polymers that have higher cross-linking and lower sulfonation is increased more, especially at the initial time.
- The networks of both groups examined are different. The PS wastes were incorporated into the whole network to an extent of 15–35%.

Such investigations could contribute to the utilization of wastes of PS in the direction of sorbents and especially if the PS wastes are contaminated with other polymers.

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Received March 28, 1994

Accepted August 12, 1994