

# Synthesis of Macroporous Bifunctional Ion Exchangers Containing Sulfo and Carboxyl Groups

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## Synopsis

The synthesis of the macroporous copolymers which contain variable percentages of acrylonitrile or methyl methacrylate and ion exchangers, respectively, are investigated. The authors also studied the influence of the copolymerization parameters on the matrix structure as well as the sulfonation reaction with  $\text{HSO}_3\text{Cl}$ . The sulfonation process of these macroporous matrices with  $\text{HSO}_3\text{Cl}$  yields ion exchangers which contain sulfo and carboxyl groups. The total cation-exchange capacities are roughly 4.0–5.0 meq/g.

During the last 10 years there has been an increasing interest in the field of styrene–divinylbenzene copolymers as porous packing material for chromatography, or polymeric matrix for a large number of ion exchangers.<sup>1–3</sup>

The experimental conditions used for the formation of the macroporous matrix influence the copolymer structure and, consequently, the kinetic and equilibrium properties of the ion exchangers.<sup>1</sup> Adding different inert compounds, “so-called diluents,” to the copolymerization mixture (styrene and divinylbenzene) yields the new types of matrices.<sup>1</sup> Evidently, the properties of these new matrices depend on the amount of the diluent, its chemical structure, and content of divinylbenzene (%).<sup>2</sup>

In order to improve the behavior of the packing materials for chromatography or the hydrophilic properties of the ion exchangers using the gel matrices, the literature mentions the syntheses of the ternary copolymers, which contain, besides styrene and divinylbenzene (crosslinking agent), acrylic or methacrylic comonomers. The sulfonation of these copolymers leads to the sulfo–carboxylic cation exchangers having a gel type structure.<sup>4–8</sup>

The ternary copolymers and anion exchangers with the same chemical structure were later prepared.<sup>9,10</sup>

This paper deals with the synthesis and the study of the macroporous cation exchangers containing sulfo and carbonyl groups bonded on the same polymeric matrix. It also investigates the modification of acrylonitrile and ester groups during the sulfonation process.

## EXPERIMENTAL

### Preparation of the Macroporous Crosslinked Matrices and of the Ion Exchangers

The suspension copolymerization of the monomers was run in a standard suspension polymerization apparatus, consisting of 1-L, three-necked, cylindrical

round-bottomed flask fitted with a variable mechanical stirrer, a thermometer, and a reflux condenser. A solution of styrene, technical-grade divinylbenzene (51.4% divinylbenzene and 45% ethylstyrene), variable quantities of acrylonitrile or methylmethacrylate, which contained 25% polystyrene ( $\bar{M}_w = 74,000$ ) as diluent, was added to an aqueous solution of styrene-maleic anhydride copolymer ammonium salt (0.40%) and gelatin (0.10%). The mixture of monomers was stirred and the organic phase dispersed as fine droplets (0.30–1.50 mm diameter), and the copolymerization process was carried out at 80°C for about 14 hr in a thermostated water bath. The beads of copolymer were sieved, washed, dried, and then extracted with dichloromethane in a Soxhlet apparatus. The dried beads were later on sulfonated with chlorosulfonic acid. A 5:1  $\text{HSO}_3\text{Cl}$ /copolymer molar ratio was used.

### Methods of Determining Porosity and Chemical Structure

The macroporous copolymer beads were characterized in order to get information on their physical and chemical structure. For this purpose, the copolymer beads were vacuum-dried at 50°C for 24 h in order to measure the pore structure by the apparent density ( $\rho_{\text{ap}}$ ), porosity (% P), volume swollen coefficient ( $B$ ), solvent uptake coefficients, pore volume ( $V_p$ ), and surface areas ( $S$ ).

The apparent densities ( $\rho_{\text{ap}}$ ) were picnometrically measured, and the surface areas were measured by the nitrogen-adsorption method<sup>11</sup> on a Ströhlein ARFA Meter.

In order to confirm the chemical structure of the crosslinked copolymers, infrared spectroscopy was applied using KBr disk technique, because the samples were insoluble in the usual solvents and the structure of the solid had to be preserved. The best concentration was 3.0 mg sample and 100 mg KBr. Spectra were recorded on a Perkin-Elmer 577 Spectrophotometer.

A few samples of copolymers and cation exchangers were thermogravimetric characterized. The measurements were performed on the powder samples at a heating rate of 10°C/min up to 900°C, in air, on a Erdey-Paulik-Budapest Derivatograph.

The percent of nitrogen and acrylonitrile, respectively, contained by the styrene-acrylonitrile-divinylbenzene copolymers was determined using the Kjeldhal method.<sup>12</sup>

The cation-exchange capacity values of the sulfonated copolymers were determined according to the method of Dima and coworkers.<sup>13</sup> In this respect, the total cation exchange capacity  $K_T$  and the sulfonic capacity,  $K_{\text{SO}_3\text{H}}$ , were measured. The carboxylic exchange capacity  $K_{\text{COOH}}$ , could be determined by the mean of the equation,

$$K_{\text{COOH}} = K_T - K_{\text{SO}_3\text{H}} \quad (1)$$

Weighed samples of air-dried cation exchangers (2.0–2.5 g), in H-form (acid), were placed in fritted-bottom columns and 1000 mL of 0.20%  $\text{CaCl}_2$  aqueous solution was passed through the cation exchanger with a flow rate of 150 mL/h to determine the sulfonic cation-exchange capacity  $K_{\text{SO}_3\text{H}}$ . The total exchange capacity was determined according to the same manner with a 0.20%  $\text{Ca}(\text{CH}_3\text{COO})_2$  aqueous solution. The Ca-ion concentrations (in influent and effluent) were determined complexonometrically<sup>14</sup> in the presence of Eriochrom

Black T, as indicator. Simultaneously, other cation-exchanger samples were dried at 50°C, in a vacuum oven, for 24 h, to determine the moisture content (H<sub>2</sub>O%).

The solvent uptake by the copolymer samples and moisture coefficient (amount of water taken up by the vacuum-dried samples of the cation exchangers) have been determined using the centrifugation method of the swollen ion exchangers (H-form) placed in glass tubes equipped with a fritted-bottom, at 500 g, for 60 min.<sup>15</sup>

The values of the pore volume (PV), the "so-called" macroporosity ( $Q$ ), was calculated using the equation<sup>16,17</sup>

$$PV = \frac{1}{\rho_{ap}} - \frac{1}{\rho} \quad (2)$$

where  $\rho_{ap}$  is the apparent density (g/mL) and  $\rho$  is the skeletal density (g/mL), determined by the picnometric method in *n*-heptane.

The porosity (% P) was calculated according to eq. (3):

$$\% P = 100 \times (1 - \rho_{ap}/\rho) \quad (3)$$

and it represents pore % contained by the copolymers.

The swelling volume ( $B$ ) was calculated from the relationship given by Dušek,<sup>18</sup>

$$B = \rho_{ap}/\rho + (W - 1) \times \rho_{ap}/\rho_{solv} \quad (4)$$

where  $W - 1$  is the amount of solvent uptake (mL/mL), determined by the centrifugal method,<sup>15</sup> and  $\rho_{solv}$  is the density of solvent (g/mL).

The pore average diameter size was calculated according to the relationship,

$$\bar{D} = \frac{4PV}{S_{BET}} \times 10^4 \quad (5)$$

(cylindrical model assumed for the pore shape).

## RESULTS AND DISCUSSION

The main features of the macroporous copolymers prepared are listed in Table I. From Table I, it results that the third comonomer, i.e., the amount of acrylonitrile (AN) and methyl methacrylate (MeM), respectively, have a great influence on the macroporosity of the copolymers. It seems that AN favors the development of a higher macroporosity by the comparison with methacrylate. This is shown by higher values for pore volume and smaller ones for the apparent density ( $\rho_{ap}$ ). As can be seen (Table I), increasing the divinylbenzene percent, keeping constant the amount of AN (or MeM), has little influence on the copolymers features, except the  $\bar{D}$  value (experiments 6 and 7).

The macroporous copolymers with AN have larger pore diameter, while those with MeM have smaller ones.

As a general observation, it can be seen that the values of the solvent uptake (toluene and cyclohexane) depend on the amount of AN and are also larger for these copolymers.

TABLE I  
Chemical Composition and Main Features of the Polymeric Matrices Using Polystyrene ( $M_w = 7.4 \times 10^4$ ) as Diluent

Expt no.	DVB	Solvent uptake (mL/g)			Apparent density (g/mL)	AN/MeM (%)	Pore volume (mL/g)	Swollen volume $B$	$S$ (m <sup>2</sup> /g)	$D_{av}$ (Å)
		Cyclohexane	Methanol	Toluene						
1	8.0	0.97	0.10	1.39	1.0300	—	0.036	1.43	5.57	258
2	8.0	0.62	0.27	1.37	1.0254	2.00	0.041	1.40	4.13	397
3	8.0	0.58	0.54	1.37	0.7627	6.20	0.376	1.04	5.44	2765
4	8.0	0.35	0.71	1.25	0.7310	10.34	0.433	1.09	5.25	3299
5	8.0	0.37	0.81	1.22	0.7075	19.66	0.479	0.84	—	—
6	12.0	0.27	0.65	1.11	0.7391	10.12	0.418	0.78	6.42	2604
7	18.0	0.33	0.72	0.94	0.7639	10.50	0.375	0.68	7.73	1940
<u>Styrene-acrylonitrile-divinylbenzene matrix</u>										
8	8.0	0.64	0.24	1.27	1.0411	2.00	0.026	1.30	6.14	169
9	8.0	0.43	0.44	1.20	0.8360	5.00	0.261	0.97	6.50	1606
10	8.0	0.31	0.67	1.18	0.8159	10.00	0.291	0.93	5.43	2144
11	8.0	0.28	0.70	1.05	0.7962	20.00	0.321	0.79	7.79	1665
12	12.0	0.50	0.50	0.78	0.7898	10.00	0.331	0.53	8.25	1605
13	18.0	0.43	0.58	0.73	0.7895	10.00	0.332	0.35	8.57	1550
<u>Styrene-methyl methacrylate-divinylbenzene matrix</u>										

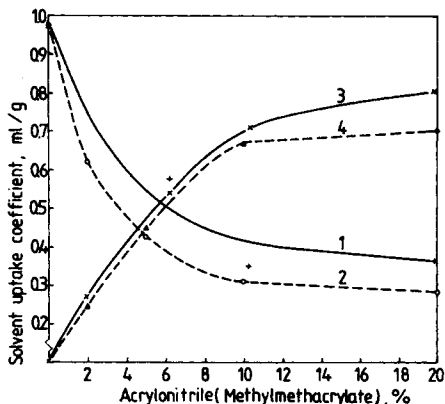


Fig. 1. Dependence of the cyclohexane (—) and methanol (---) uptake coefficients on the content of acrylonitrile (curves 1 and 3) and methyl methacrylate (curves 2 and 4) for the macroporous matrices.

As a general rule the solvent uptake data decrease while the percent of AN or MeM increases.

It can also be noticed that the values of the methanol uptake vary conversely by comparison with that for toluene or cyclohexene (Fig. 1). The values of the swollen volume ( $B$ ), as well as the apparent density ( $\rho_{ap}$ ), decrease with an increasing amount of AN or MeM while DVB content is kept constant (Fig. 2). The solvent uptake data are little influenced by the increasing of the crosslinking degree of the matrices (experiments 6, 7, and 12).

In conclusion, it can be asserted that the amount of AN influences more strongly the macroporosity, i.e., the macroporous copolymer structure, than the amount of MeM. This is also due to the diluent used, which is polystyrene, which behaves as a poor solvent against the segments of polystyrene, from the polymeric matrix, during their emergence.

Polystyrene, as diluent, interacts differently with the polymeric segments which contain acrylonitrile or methyl methacrylate units. Seidl<sup>1</sup> and co-workers pointed out the influence of the diluent nature on the porous structure of the copolymers by the polymer reciprocal effect.

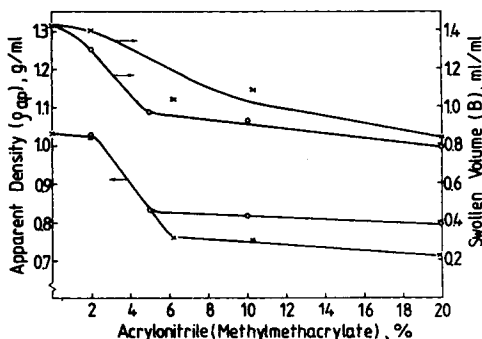


Fig. 2. Dependence of the apparent density ( $\rho_{ap}$ ) and swollen volume ( $B$ ) on the content of acrylonitrile or methyl methacrylate for St-AN-DVB (curves 1 and 3) and St-Me-DVB (curves 2 and 4) macroporous copolymers.

TABLE II  
Values of Exchange Capacities and Moisture Holding Coefficient of the Bifunctional Cation Exchangers<sup>a</sup>

Expt no.	Exchange capacity (meq/g)			Moisture holding coefficient (% H <sub>2</sub> O)
	$K_{\text{SO}_3\text{H}}$	$K_{\text{COOH}}$	$K_T$	
1	5.07	—	5.08	42.00
2	4.46	0.29	4.75	29.00
5	4.01	0.44	4.45	20.00
7	3.79	0.29	4.08	17.00
9	4.73	0.17	4.89	44.00
10	4.36	0.19	5.12	39.00
11	4.03	0.22	4.25	37.00
12	4.23	0.13	4.36	33.00
13	3.99	0.38	4.39	21.00

<sup>a</sup> Copolymer/HSO<sub>3</sub>Cl molar ratio = 1:5; 20°C; 5 h.

A few samples of copolymers underwent the sulfonation reaction, using HSO<sub>3</sub>Cl, at 20°C, for 5 h. The cation exchangers prepared contain sulfo and carboxyl groups, and they are the so-called "bifunctional cation exchangers." The total exchange capacity  $K_T$  is obtained from the relationship

$$K_T = K_{\text{SO}_3\text{H}} + K_{\text{COOH}} \quad (6)$$

The sulfonation process of the ternary macroporous copolymers is intricate, because chlorosulfonic acid reacts with the aromatic rings and simultaneously with the nitrile, or ester, groups bonded to the main polymeric chain, yielding sulfo-carboxylic cation exchangers. The exchange capacity measured is given in Table II.

The authors were interested to learn what happened particularly with the nitrile and ester groups during the sulfonation process. For this reason an IR study on the copolymers and cation exchangers was performed. A full IR study concerning the styrene-divinylbenzene matrix and its ion exchangers was performed by Lindeman.<sup>19</sup> In this case, the authors investigated only the chemical transformation of the nitrile, or ester, groups, as well as the sulfonic acid formation.

TABLE III  
Nitrogen Content of the St-AN-DVB Macroporous Copolymers and Bifunctional Cation Exchangers

Expt no.	Nitrogen (%)	
	Copolymer	Bifunctional cation exchangers
4	2.73	1.51
4 <sup>a</sup>		1.13
5	5.19	2.44
5 <sup>a</sup>		2.01
7	2.77	1.46
7 <sup>a</sup>		1.35

<sup>a</sup> Samples were sulfonated with a copolymer/HSO<sub>3</sub>Cl molar ratio of 1:5, at 72°C for 5 h.

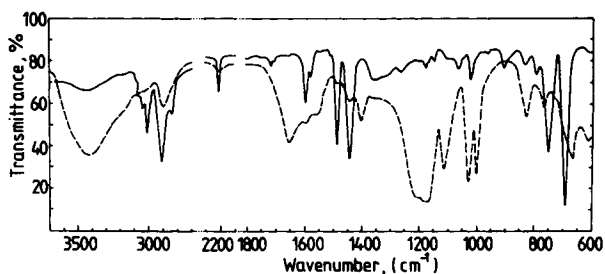


Fig. 3. IR spectra of St-AN-DVB matrix (1) and its bifunctional cation exchangers (2)—sample 5.

First of all, the parameters of the sulfonation process with  $\text{HSO}_3\text{Cl}$  did not transform fully all the nitrile and ester groups into carboxyl groups.

The bifunctional cation exchangers prepared from St-AN-DVB still contain nitrogen, even if the sulfonation process is performed at  $75^\circ\text{C}$  (Table III). As a general rule, the carboxylic exchange capacity values, experimentally measured, are smaller than those calculated, according to the polymeric chemical structure. This means that only a part of the nitrile or ester groups was transformed under the chlorosulfonic acid action (Figs. 3 and 4).

The presence of the sulfonic group is given by a frequency band ( $1200\text{ cm}^{-1}$ ) unusually broad (about  $100\text{ cm}^{-1}$ ). The frequency band at  $670\text{ cm}^{-1}$  assigned to  $\gamma\text{ C—S}$  vibration also has to be mentioned. The frequency vibration from  $830\text{ cm}^{-1}$  is assigned to the aromatic ring vibrations, parasubstituted with  $\text{—SO}_3\text{H}$  groups.

Both IR spectra also contain frequency bands which could be assigned to  $\gamma\text{ C=O}$  ( $1580, 1600, 1660\text{ cm}^{-1}$ ) and  $\gamma\text{ C—O}$  ( $1200\text{--}1270\text{ cm}^{-1}$ ) vibrations. But also the frequency  $\gamma\text{ C=O}$  could be assigned to the amide group, yielding from  $\text{—C}\equiv\text{N}$  ones under the action of  $\text{HSO}_3\text{Cl}$ .

The absorption at  $2230\text{ cm}^{-1}$  assigned to the  $\gamma\text{ C}\equiv\text{N}$  stretching vibration shows distinctly the presence of the acrylonitrile units, both in copolymer and in the bifunctional cation exchangers. The amount of the acrylonitrile meric units contained by the cation exchanger is smaller, about 1.10–2.44% nitrogen (Fig. 3; Table III).

A relatively strong and broad adsorption band appears at  $3200\text{--}3600\text{ cm}^{-1}$ , and it could be assigned to the molecules of water which participate in the formation of the H bonds (Figs. 3 and 4).

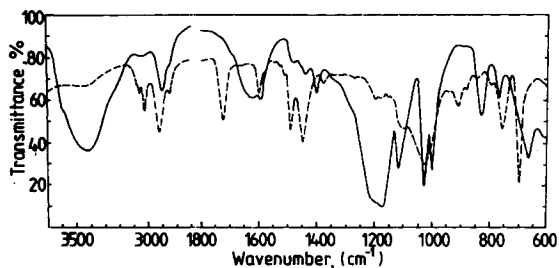
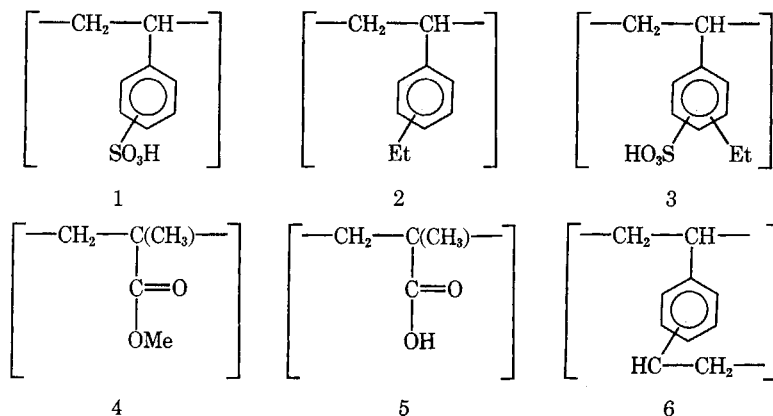


Fig. 4. IR spectra of St-MeM-DVB matrix (1) and its bifunctional cation-exchangers (2)—sample 11.



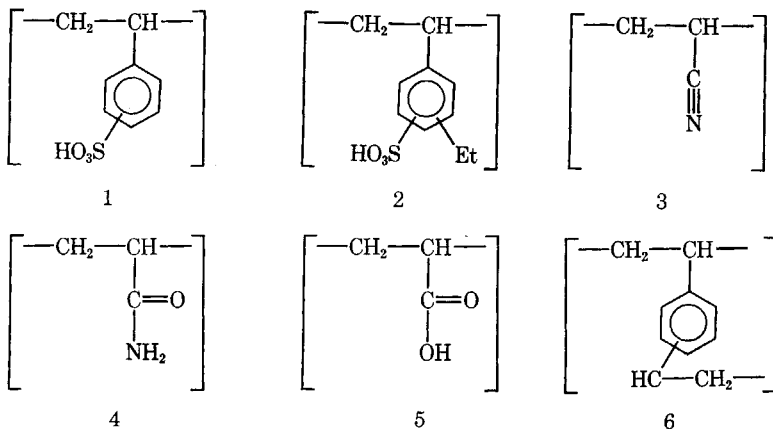
Bifunctional Cation Exchangers Based on Styrene-Methyl methacrylate-Divinylbenzene Matrix

Expt no.	Structural unit (%)					
	1	2	3	4	5	6
10	64.59	1.36	7.40	13.36	3.14	10.15
11	52.92	0.46	7.50	26.67	3.30	9.22

Scheme A. Percentage Composition of the Meric Units in 100 Structural Units of Macroporous Bifunctional Cation Exchangers

Taking into account the chemical composition and the structural modification which take place during the sulfonation process, the authors tried to assume that the bifunctional cation exchangers could have the structures, shown in Schemes A and B.

The authors, having in mind the above structures, also tried to calculate the



Bifunctional Cation Exchangers Based on Styrene-Acrylonitrile-Divinylbenzene Matrix

Expt no.	Structural unit				
	1	2	3 + 4	5	6
4	60.45	8.77	16.73	4.50	9.45
5	50.09	8.81	25.60	6.46	9.03

Scheme B. Percentage Composition of the Meric Units in 100 Structural Units of Macroporous Bifunctional Cation-Exchangers



TABLE IV  
Dependence of Activation Energy on Composition of Copolymers and Bifunctional Cation Exchangers

Expt no.	DVB (%)	Activation energy (kcal/mol), decomposition stages	
		I	II
		<u>Copolymers</u>	
1	8.0	55.7	132.9
4	8.0	59.0	221.5
5	8.0	66.4	—
7	18.0	70.4	—
		<u>Bifunctional Cation-Exchangers</u>	
4	8.0	35.5	80.7
5	18.0	39.2	93.3

percent of the meric units included in 100 units, employing the gravimetric composition (the number of the meric units in 100 g of bifunctional exchanger<sup>20</sup>).

The structure that is the variation of the structural meric unit number in 100 structural units is rather important, and it gives details concerning the conversion degree of the polymeric matrices.

A few samples of the macroporous copolymers and bifunctional cation exchangers were searched from the thermal behavior point of view, and the activation energy was calculated.<sup>21</sup> The activation energy data are listed in Table IV.

Some conclusions concerning the thermal behavior of the matrices and cation exchangers can be drawn.

1. The activation energy corresponding to the two decomposition stages increases simultaneously with the increasing of the crosslinking agent percent. The activation energy values are higher for the polymeric matrices than that of the bifunctional cation exchangers.

2. The matrices have a higher thermal stability than the bifunctional cation exchangers.

3. The chemical transformation which the polymeric matrices promotes weakened the thermal resistance of the macroporous copolymers due to the grafting of the sulfo and carboxyl groups on the main chain. The ionic groups are the first ones on which decomposition starts.

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